

Structure–Property Relationships in Trimethylenemethane-Type Biradicals. 2. Synthesis and EPR Spectral Characterization of Dinitroxide Biradicals[†]

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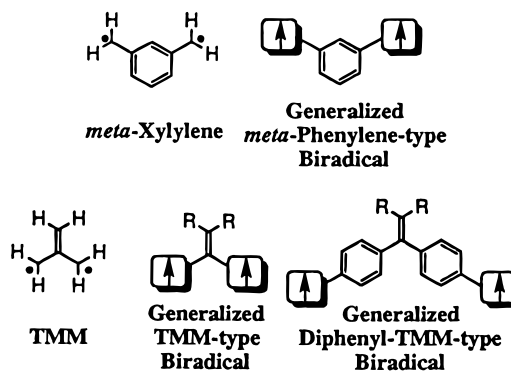
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Several trimethylenemethane-type (TMM-type) dinitroxide biradicals have been prepared that differ in *tert*-butylaminoxylphenyl ring torsion angles by virtue of different steric demands of their “spin-protecting groups”. In addition, the synthesis of a TMM-type dinitroxide having a planar π -system is reported. The synthetic route employed for the planar TMM-type biradical is general and should therefore expand the utility of TMM-type biradicals that are susceptible to bond torsions that attenuate exchange coupling. The compounds presented are designed to be effective to map out *J*-coupling/conformation space in TMM-type biradicals. EPR spectroscopic parameters (hfcc and *D*-values) were compared to determine if their values reflected differences in conformation in the series of biradicals. Interestingly, neither N- nor H-hfcc varied within our series of biradicals/monoradicals in a regular fashion, indicating that there is no apparent relationship between N- or H-hfcc and conformation (as judged by molecular mechanics calculations). However, *D*-values, estimated from relative intensities of $\Delta m_s = 1$ and $\Delta m_s = 2$ transitions, are consistent with a varied degree of delocalization in the dinitroxides: smaller *D*-values for biradicals having smaller aryl torsions (and greater delocalization), and larger *D*-values for dinitroxides having greater aryl torsions (and less delocalization). All the biradicals studied, except **5**^{••}, exhibited linear Curie plots. The linear Curie plots are consistent with both triplet ground-states and singlet–triplet degeneracies. Interestingly, dinitroxide **6**^{••} exhibited a linear Curie plot, despite the lack of a π -coupling fragment. Biradical **5**^{••}, however, is a ground-state singlet species with the triplet lying about 140 cal/mol above the singlet.

Introduction

Large amplitude bond torsions can dramatically affect exchange couplings in organic biradicals when the bonds connect spin-containing groups to exchange-coupling fragments. Several examples of this structure–property relationship have been noted for *m*-phenylene-type biradicals.¹ Trimethylenemethane-type (TMM-type) biradicals having the 1,1-diarylethene moiety are an interesting class of molecules with which to study this phenomenon because diarylethene conformation and dynamics have been elucidated.²



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[†] Part 1: Shultz, D. A.; Boal, A. K.; Farmer, G. T. *J. Am. Chem. Soc.* **1997**, *119*, 3846; Part 3: Shultz, D. A.; Boal, A. K.; Bourbeau, M. P.; Farmer, G. T. *J. Am. Chem. Soc.*, to be submitted.

(1) For papers discussing the effects of torsion on exchange coupling in *m*-phenylene-type biradicals, see: (a) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180. (b) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847. (c) Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273. (d) Okada, K.; Matsumoto, K.; Oda, M.; Murai, H.; Akiyama, K.; Ikegami, Y. *Tetrahedron Lett.* **1995**, *36*, 6693. (e) Adam, W.; van Barneveld, C.; Bettle, S. E.; Engert, H.; Hanson, G. R.; Harrer, H. M.; Heim, C.; Nau, W. M.; Wang, D. *J. Am. Chem. Soc.* **1996**, *118*, 3974. (f) Fujita, J.; Tanaka, M.; Suemune, H.; Koga, N.; Matsuda, K.; Iwamura, H. *J. Am. Chem. Soc.* **1996**, *118*, 9347. (g) Okada, K.; Imakura, T.; Oda, M.; Murai, H.; Baumgarten, M. *J. Am. Chem. Soc.* **1996**, *118*, 3047. (h) See also ref 11. (i) Ab initio calculations explain antiferromagnetic coupling in certain *m*-phenylene-linked structures, see: Fang, S.; Lee, M.-S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1995**, *117*, 6727.

(2) Kaftory, M.; Nugieli, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8181.

1,1-Diphenylethene adopts a nonplanar geometry due to steric interactions between the phenyl rings. The minimum energy geometry is computed to have phenyl torsion angles, ϕ , of ca. 30°. Increased phenyl torsion exists in 2,2-disubstituted structures because of additional steric interactions. The chiral, C_2 -symmetric conformer of 1,1-diphenylethene rapidly equilibrates with its enantiomer by the zero- and one-ring flip mechanisms.^{2,3}

If the phenyl rings of 1,1-diphenylethene are substituted in the *para*-positions with $S = 1/2$ (paramagnetic) functional groups, as illustrated above, the biradical produced is expected to be a ground-state triplet

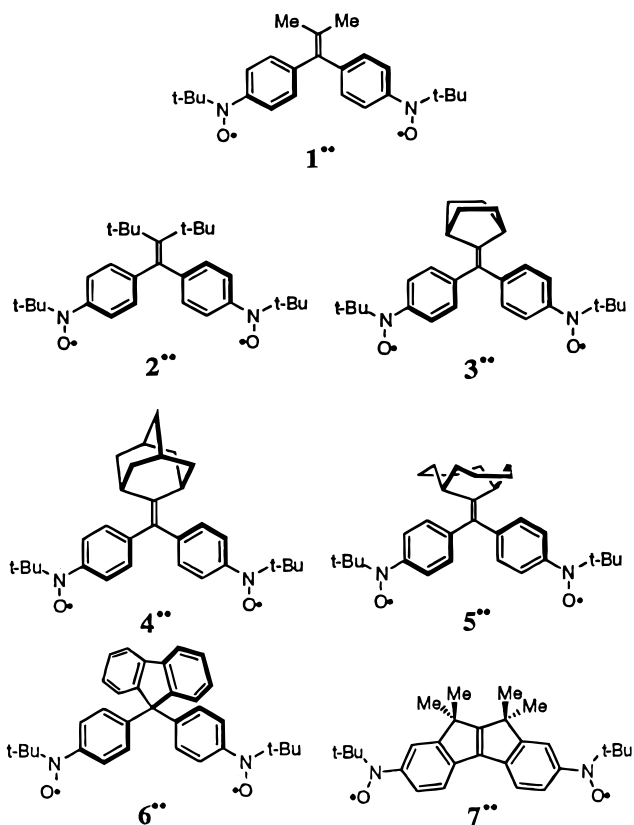
(3) Phenyl torsions in substituted 1,1-diphenylethenes are fast on the NMR time scale even at –90 °C, see: Rabinovitz, M.; Agranat, I.; Bergmann, E. D. *Isr. J. Chem.* **1969**, *7*, 795.

based on π topology,^{4–8} and the 1,1-diphenylethene moiety is a TMM-type exchange coupling fragment. The effectiveness of this exchange coupler is strongly correlated to the magnitude of phenyl torsion since phenyl torsion modulates spin density in the ethene unit. That is, the greater the delocalization of spin into the ethene fragment, the greater the stabilization of the triplet state.

We studied a few 1,1-diarylethene-TMM-type bis-(phenoxy) radicals and found fundamental structure–property relationships for spin–spin coupling in this class of biradicals.^{9–11} As surmised, steric interaction between structural elements of the bis(phenoxy) biradicals has the effect of increasing the torsion angles, ϕ , of the aryl groups and modulating exchange couplings.

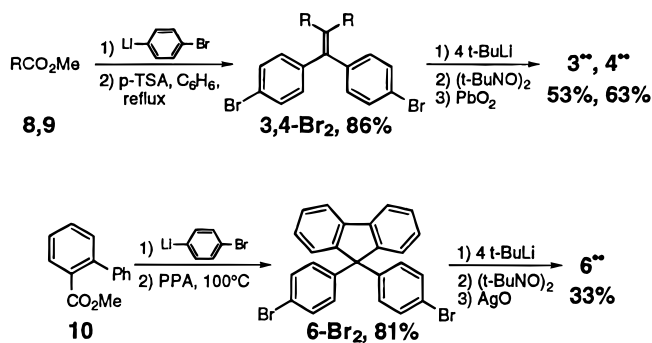
Since nitroxide radicals are useful for the construction of coordination polymers that order magnetically,¹² we wish to study the relationship between conformation and exchange coupling in a series of isolated dinitroxide molecules, and correlate our findings with structure–property relationships in coordination polymers using the same dinitroxides. Ultimately, we endeavor to determine whether crystal packing forces or coordination polymer geometric requirements can alter biradical conformation, and therefore biradical exchange coupling. If so, molecular building blocks having “unfavorable” conformations (vide infra) might be more useful for the construction of solid-state coordination polymers with higher ordering temperatures than might otherwise be expected. In addition to this interest, we are excited about the possibility of generating a series of biradicals having a variety of torsion angles and correlating spin–spin coupling with conformation.^{9–11}

Along these lines, we report here the synthesis and solution EPR spectral characterization of a series of TMM-type dinitroxides, **1****–**5**** and **7****, designed to have a range of aryl torsion angles, as well as a model biradical, **6****.



Results

Synthesis. Dinitroxide **1**** was prepared as described previously,¹³ and **3**** and **4**** were prepared in a similar fashion as shown below. Methyl norbornane-7-carboxylate (**8**)¹⁴ and methyl adamantane-2-carboxylate (**9**)⁹ were reacted with 4-lithiobromobenzene, and the resulting carbinols were subsequently dehydrated to yield dibromides **3-Br₂** and **4-Br₂**, respectively. Fluorenyl-dibromide **6-Br₂** was prepared in a similar fashion, except that the intermediate alcohol was reacted with poly[phosphoric acid] to generate the fluorene moiety. All dibromides were converted to the corresponding dinitroxides using standard protocols.¹³



Biradicals **2**** and **5**** required a different approach due to the greater steric demands of the di-*tert*-butylmethylenes and bicyclo[4.4.1]undecyl groups, and we chose the

(4) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(5) Berson, J. A. *Diradicals*; Wiley: New York, 1982.

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

(7) Iwamura, H. *Pure Appl. Chem.* **1987**, *59*, 1595.

(8) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(9) Shultz, D. A.; Boal, A. K.; Farmer, G. T. *J. Am. Chem. Soc.* **1997**, *119*, 3846.

(10) Shultz, D. A.; Boal, A. K.; Bourbeau, M. P.; Farmer, G. T. *J. Am. Chem. Soc.*, to be submitted.

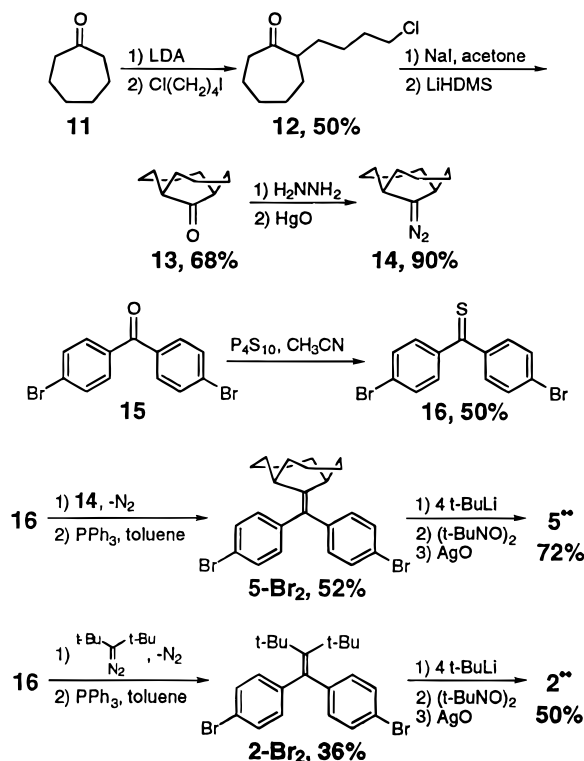
(11) Shultz, D. A. In *Magnetic Properties of Organic Materials*, P. Lahti, Ed.; Marcel Dekker: New York, in press.

(12) For papers on nitroxide complexes, see the following: (a) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392. (b) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Chem. Mater.* **1992**, *4*, 204. (c) Gatteschi, D.; Sessoli, R. *J. Magn. Magn. Mater.* **1992**, *104*, 2092. (d) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447. (e) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635. (f) Luneau, D.; Laugier, J.; Rey, P.; Ulrich, G.; Ziessel, R.; Legoll, P.; Drillon, M. *J. Chem. Soc., Chem. Commun.* **1994**, 741. (g) Kitano, M.; Koga, N.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1994**, 447. (h) Kitano, M.; Ishimaru, Y.; Inoue, K.; Koga, N.; Iwamura, H. *Inorg. Chem.* **1994**, *33*, 6012. (i) de Panthou, F. L.; Belorizky, E.; Calemczuk, R.; Luneau, D.; Marcenat, C.; Ressouche, E.; Turek, P.; Rey, P. *J. Am. Chem. Soc.* **1995**, *117*, 11247. (j) Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803. (k) Pei, Y.; Kahn, O.; Ouahab, L. *Inorg. Chem.* **1996**, *35*, 193. (l) Iwamura, H.; Inoue, K.; Hayamizu, T. *Pure Appl. Chem.* **1996**, *68*, 243. (m) Ottaviani, M. F.; Turro, C.; Turro, N. J.; Bossman, S. J.; Tomalia, D. *J. Phys. Chem.* **1996**, *100*, 13667. (n) Sokolowsky, A.; Bothe, E.; Bill, E.; Weyhermueller, T.; Wieghardt, K. *Chem. Commun.* **1996**, 1671. (o) Nakatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161. (p) Fegy, K.; Luneau, D.; Ohm, T.; Paulsen, C.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1270.

(13) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952.

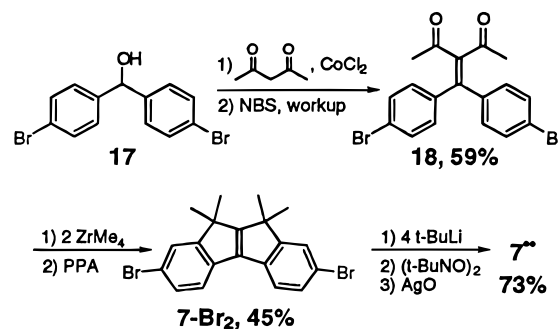
(14) Kwart, H.; Kaplan, L. *J. Am. Chem. Soc.* **1954**, *76*, 4072.

Barton–Kellogg reaction^{15,16} for synthesis of dibromides **2-Br₂** and **5-Br₂**. This route required the preparation of diazo compounds **14** and di-*tert*-butyldiazomethane,¹⁷ as well as 4,4'-dibromothiobenzophenone,¹⁸ **16**, as outlined below. Diazoalkane **14** was prepared from bicyclic ketone **13**, which in turn was prepared by intramolecular alkylation of the enolate formed from 2-(4'-iodobutyl)cycloheptanone. This iodide was prepared from the corresponding chloride, **12**, which was the alkylation product of cycloheptane enolate reacted with 4-chloro-1-iodobutane.



The planar TMM-type biradical, **7****, was prepared as shown below. Bis(4-bromophenyl)methanol, **17**, was reacted with acetylacetone in the presence of anhydrous cobaltous chloride,¹⁹ followed by bromination with NBS, and workup-induced elimination to give conjugated enedione **18**. Dione **18** was converted into an intermediate diol by reaction with 2 equiv of tetramethylzirconium.^{20,21} Ring-closure to indeno[1,2-*a*]indene derivative **7-Br₂** was affected by stirring the diol with poly[phosphoric acid] at 147 °C. The biradical was prepared using conditions described for the other dinitroxides.

The procedures used to generate the hydroxylamine/nitroxide functionality also gave mononitroxide radicals



(**1****–**7****) in all cases. Mass spectral analysis indicated that these molecules lacked bromine atoms.

Cross conjugated dinitroxides such as **1****–**5**** are red solids, giving red-colored solutions, and the electronic absorption spectrum of **2**** in Figure 1 is typical. Interestingly, **7**** is a beautiful purple color and gives purple solutions. Consistent with the electronic and conformational changes resulting from the planarized chromophore, the longest wavelength visible absorption band of **7**** is red-shifted ca. 30 nm (ca. 1825 cm⁻¹) and hyperchromically shifted compared to that of **2**** as shown in Figure 1.

Molecular Mechanics Calculations.^{11,22} MM2²³ minimized structures for *i*-propyldiphenylmethane, 1,1-diphenyl-2,2-di-*tert*-butylethene, diphenylmethylenenorbornane, diphenylmethyleneadamantane, diphenylmethylenebicyclo[4.4.1]undecane, and 9,9-diphenylfluorene as well as pertinent bond angles and torsion angle values are shown in Figure 2. For the diphenylethylenes listed, phenyl torsion increased in the series: diphenylmethylenenorbornane < *i*-propyldiphenylmethane < diphenylmethyleneadamantane < diphenylmethylenebicyclo[4.4.1]undecane < 1,1-diphenyl-2,2-di-*tert*-butylethene. The steric demand of the bicyclic or tricyclic “protecting group” increases as the valence angle θ increases causing ϕ to increase in the same order. Of course these arguments and results do not apply to 3,12-dihydro-3,3,12,12-tetramethylindeno[1,2-*a*]indene, a polycyclic molecule in which phenyl torsion is precluded by fusion of the *gem*-alkyl groups to the phenyl rings.

Fluid-Solution EPR Spectroscopy. Figure 3 shows the EPR spectra of **1****–**7**** as solutions in toluene recorded at 298 K along with simulations.²⁴ The experimental spectra are best reproduced when a small amount of monoradical is included in the simulation. We presume that the monoradical impurity appears during sample preparation and storage since satisfactory magnetic moments were found for the biradicals. The EPR spectra were also concentration independent, ruling out the formation of dimers as the impurities. Nominal hyperfine coupling constants (hfcc) and biradical purities, estimated by simulation, are given in Table 1. Temperature-dependent spectral changes due to conformational modu-

(15) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045.

(16) Barton, D. H. R.; Guziec, F. S.; Shahak, I. J. *J. Chem. Soc. Perkin Trans. 1* **1974**, 1794.

(17) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.

(18) Scheeren, J. W.; Ooms, P. H. J.; Nivard, R. J. F. *Synthesis* **1973**, 149.

(19) Marquez, J.; Moreno-Mañas, M. *Chem. Lett.* **1981**, 173. Direct formation of ene-dione **18** by condensation of ketone **15** and acetylacetone according to the method of Lehnert failed (Lehnert, W. *Tetrahedron* **1973**, *29*, 635). However, this method was for Knoevenagel reaction of diethyl malonate and benzophenone derivatives.

(20) Majetich, G.; Lowery, D.; Khetani, V.; Song, J.-S.; Hull, K.; Ringold, C. *J. Org. Chem.* **1991**, *56*, 3988. Reaction of ene-dione **18** with the methylcerium reagent formed from methyl lithium and ceric chloride (Imamoto, T.; Takiyama, N.; Nakamura, K. *Tetrahedron Lett.* **1985**, *26*, 4763) gave only very small amounts of the desired diol.

(21) Jung, A.; Retz, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4833.

(22) Crystal structures of **1-Br₂**–**6-Br₂** have been determined and will be reported elsewhere. The crystal structures of the dibromides corroborate the MM2 results presented here. For a preliminary account, see ref 11.

(23) Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395.

(24) Fluid solution EPR spectra were simulated using the EPR Calculations for MS-Windows NT/95, Version 0.96, Public EPR Software Tools, National Institute of Environmental Health Sciences, National Institutes of Health, Research Triangle Park, NC.; Dave Duling, 1996. The correlation coefficient for the simulations are $R \geq 0.995$.

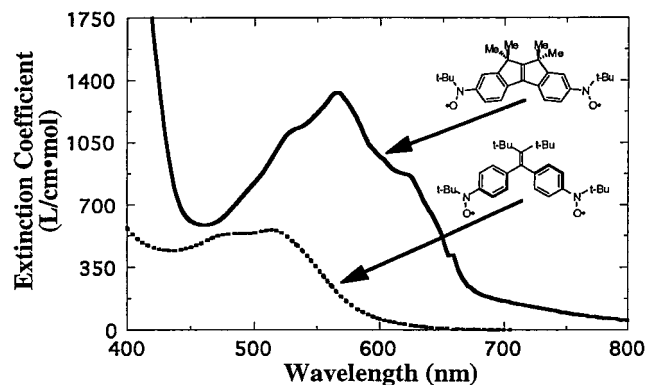


Figure 1. Electronic absorption spectra of biradicals **2**** (—) and **7**** (---) as solutions in CH_2Cl_2 .

lation of exchange²⁵ could account for the spectral appearance, but were not observed.²⁶ All biradical spectra are typical for $S = 1$ species in which the exchange interactions are much greater than hyperfine interactions ($|J| \gg |a|$).^{27,28} Hyperfine coupling constants for the monoradicals, **1–7***, are given in Table 2.

Frozen-Solution EPR Spectroscopy. Figure 4 shows the $\Delta m_s = 1$ EPR spectra of **1**–7**** recorded at 77 K in a toluene matrix. Spectra are consistent with randomly oriented triplet species,²⁹ and are typical for dinitroxides having small D -values and hyperfine structure in the $\Delta m_s = 1$ region.^{30,31} These spectral features, unfortunately, preclude our simulating the spectra. As shown in Figure 5, all biradicals exhibited $\Delta m_s = 2$ transitions, signatures of high-spin states, in which the parallel component of the nominal N-hfcc was approximately one-half that of a nitroxide monoradical (monoradical $a_{N,||} \approx 56$ G; **7**** does not exhibit hfc in the $\Delta m_s = 2$ transition), again consistent with $|J| \gg |a|$. At this time, we cannot explain the lack of hyperfine structure in the $\Delta m_s = 2$ transition of **7****. The zero-field-splitting (ZFS) parameters, $|D/hc|$, calculated from the relative intensities of $\Delta m_s = 1$ and $\Delta m_s = 2$ transitions³² are given in Table 1.

Curie plots for the doubly integrated $\Delta m_s = 2$ signals of **1**–4****, **6****, and **7**** in toluene are shown in Figure 6. The signal intensities increase linearly with increasing inverse absolute temperature, consistent with both high-spin coupling of the nitroxide units, and singlet–triplet degeneracies, i.e., $J \geq 0$.³³

The Curie plot for biradical **5**** was quite different than those of the other biradicals studied, and is shown in

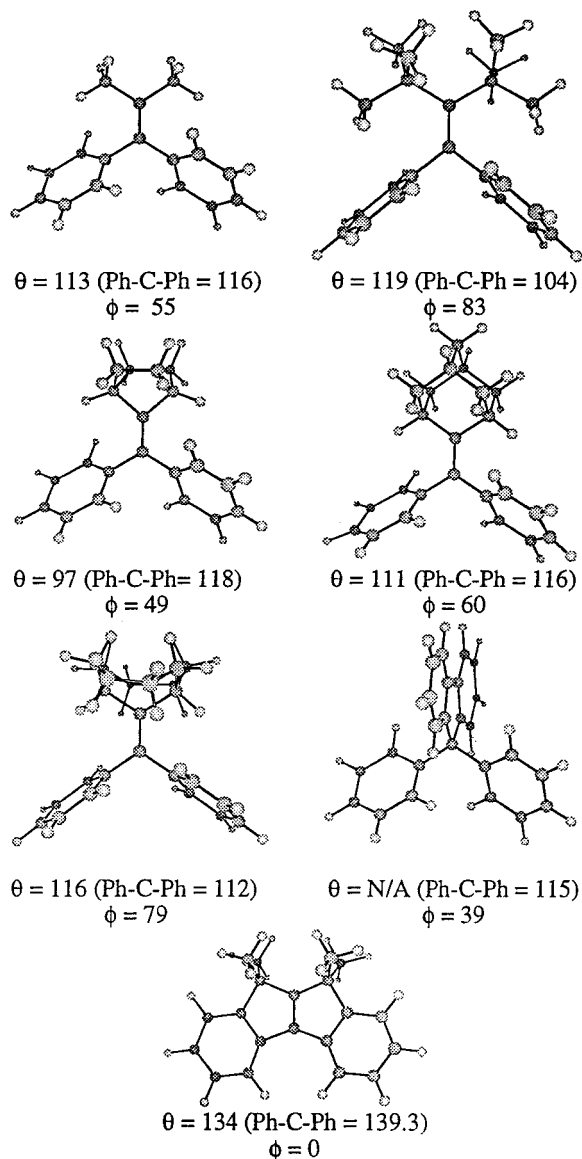


Figure 2. MM2-minimized structures for *i*-propyldiphenylmethane, 1,1-diphenyl-2,2-di-*tert*-butylethane, diphenylmethylenenorbornane, diphenylmethyleneadamantane, diphenylmethylenebicyclo[4.4.1]undecane, 9,9-diphenylfluorene, and 3,3,12,12-tetramethyl-3,12-dihydroindeno[1,2-*a*]indene. θ describes the $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^2}\text{--C}_{\text{sp}^3}$ “protecting group” bond angle, and ϕ is the phenyl torsion angle.

(25) J -modulation can cause the “alternating linewidth effect,” see refs 46–48.

(26) We thank Professor Malcolm Forbes for a copy of his program for simulating J -modulated EPR spectra.

(27) Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood PTR Prentice Hall: New York, 1993.

(28) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986.

(29) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(30) Mitsumori, T.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 2467.

(31) Akita, T.; Mazaki, Y.; Kobayashi, K. *Tetrahedron Lett.* **1995**, *36*, 5543.

(32) Weissman, S. I.; Kothe, G. *J. Am. Chem. Soc.* **1975**, *97*, 2537. $(I_{m_s=1})/(I_{m_s=2}) = [(H_{m_s=2})/D]^2$, where $I_{m_s=1}$ ($I_{m_s=2}$) is the intensity of the $\Delta m_s = 1$ ($\Delta m_s = 2$) transition, $H_{m_s=2}$ is the field at which the $\Delta m_s = 2$ transition occurs, and D is the zero-field-splitting parameter.

(33) A linear Curie plot is also consistent with degenerate singlet and triplet states. For an excellent discussion of the salient features of the Curie plot, see: *The Chemistry of Quinonoid Compounds*; Berson, J. A., Ed.; John Wiley & Sons: New York, 1988; Vol. II, p 482. In addition, linear Curie plots can also result for small negative J -values.

Figure 7. The data were fit according to the equation:³³

$$I_{\text{EPR}} = \frac{C}{T} \left[\frac{3 \exp\left(\frac{-2J}{RT}\right)}{1 + 3 \exp\left(\frac{-2J}{RT}\right)} \right]$$

where C is a constant and J is the exchange parameter. Best fit results give $J = -68 \pm 6$ cal/mol.

Discussion

Molecular Design Elements. TMM-type *spin-containing units* have been used to explore exchange coupling through sp^3 -hybridized coupling fragments and aromatic rings;^{6,34–37} however, high-spin molecules having a TMM-type exchange coupling unit are rare com-

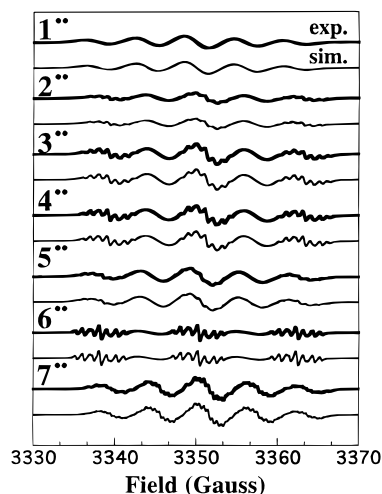


Figure 3. X-band EPR spectra (thick trace) and simulations (thin trace) of biradicals **1****–**7**** as solutions in toluene at 298 K.

Table 1. EPR Spectral Parameters for Biradicals **1**–**7******

biradical	%biradical ^a	a_N/G^b	$a_H(\text{ortho})/G^{b,c}$	$a_H(\text{meta})/G^{b,d}$	$ D /hc/cm^{-1} e$
1** ^f	100	5.95	—	—	0.0042
2**	96.35	5.82	1.37	0.63	0.0064
3**	90.65	5.95	1.01	0.40	0.0035
4**	92.01	5.99	1.10	0.44	0.0041
5**	95.73	5.98	1.13	0.90	0.0062
6**	89.10	5.88	1.12	0.58	0.0046
7**	100	6.02	1.16, 0.97	0.50	0.0035

^a Simulation includes corresponding monoradical if % biradical \neq 100. ^b Hyperfine values are actually $a/2$; estimated by spectral simulation.²⁴ ^c Protons ortho to nitroxide group. ^d Protons meta to nitroxide group. ^e D -value parameters estimated from relative intensities of $\Delta m_s = 1$ and $\Delta m_s = 2$ transitions.³² ^f 1H -hyperfine not observed in biradical; quality of spectral simulation not improved by additional hyperfine.

Table 2. EPR Spectral Parameters for Monoradicals **1*–**7***^a**

monoradical	a_N/G	$a_H(\text{ortho})/G^b$	$a_H(\text{meta})/G^c$
1*	12.00	2.10	0.90
2*	11.93	2.09	0.92
3*	11.98	2.09	0.91
4*	12.03	2.09	0.90
5*	12.08	2.08	0.88
6*	12.00	2.05	0.89
7*	12.13	2.03, 2.16	0.91

^a Hyperfine values determined by spectral simulation.²⁴ ^b Protons ortho to nitroxide group. ^c Protons meta to nitroxide group. compared to those based on *m*-phenylene linkers.^{38,39} The major advantage to using the TMM coupler is that the parent biradical has a larger singlet–triplet gap (14.5 kcal/mol)⁴⁰ than *m*-xylylene (9.2 ± 0.2 kcal/mol)⁴¹. Thus, the TMM coupler is an inherently stronger exchange coupler.

(34) Jacobs, S. J.; Dougherty, D. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1104.

(35) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744.

(36) West, A. P., Jr.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 1452.

(37) Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273.

(38) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(39) Nau, W. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2445.

(40) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.

(41) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354.

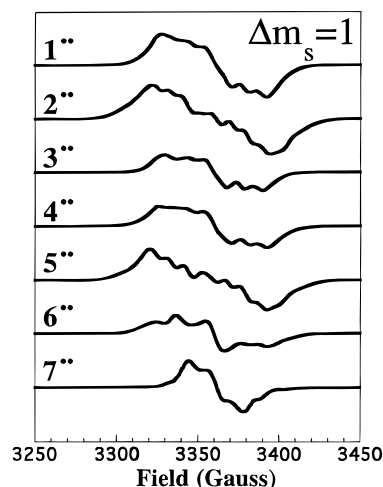


Figure 4. X-band EPR spectra ($\Delta m_s = 1$ transitions) of biradicals **1****–**7**** as frozen solutions in toluene at 77 K.

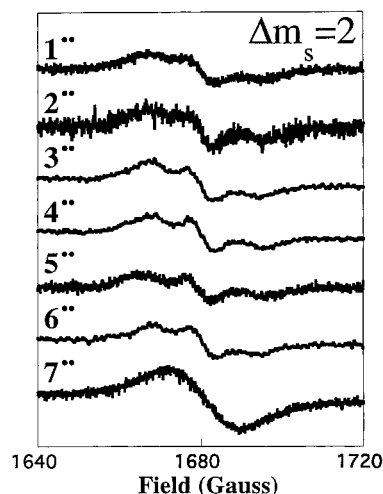


Figure 5. X-band EPR spectra ($\Delta m_s = 2$ transitions) of biradicals **1****–**7**** as frozen solutions in toluene at 77 K.

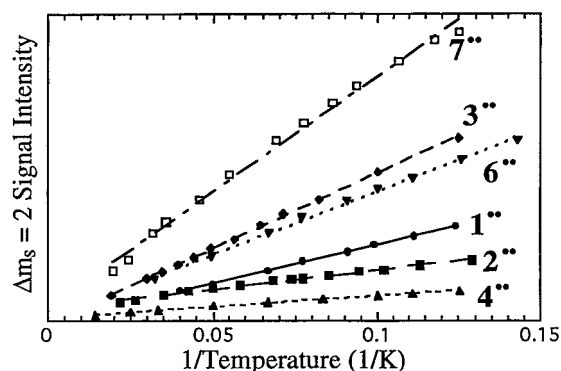


Figure 6. Curie plots for biradicals **1****–**7****. The data points were collected between ca. 8 and ca. 50 K and represent normalized signal intensities obtained by double integration of the $\Delta m_s = 2$ signal.

Design elements of a generalized diphenyl-TMM-type biradical are shown below. First, spin-containing units are attached *geminal* to an ethene moiety to complete the TMM π -topology. Second, if stable molecules are desired, a “spin-protecting group” that sterically protects unpaired electrons is necessary for biradicals having spin-delocalization into the ethene group. However, this

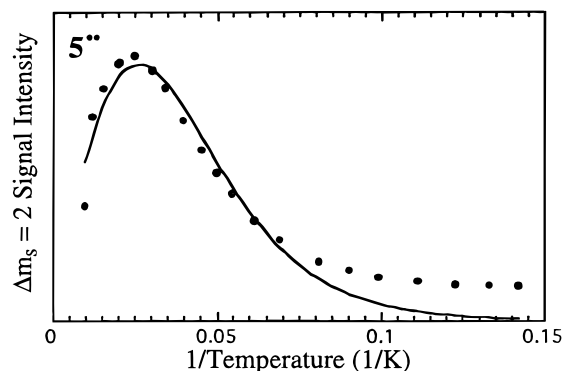
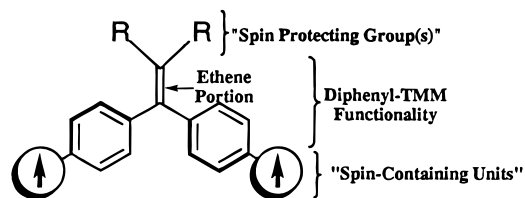


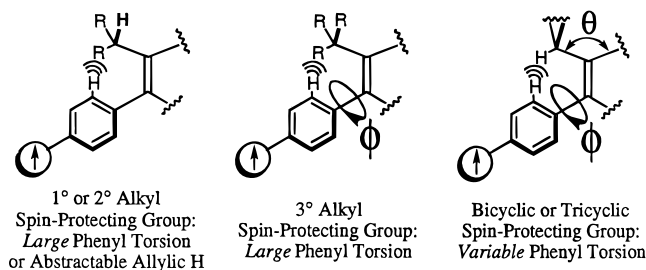
Figure 7. Curie plot for biradical $5^{\bullet\bullet}$. The data points were collected between 7 and 100 K and represent normalized signal intensities obtained by double integration of the $\Delta m_s = 2$ signal.

necessity creates a potential problem—steric interactions between atoms in the spin-protecting functionality and those in the spin-containing unit might disrupt conjugation between the spin-containing units and the ethene group. As noted in the Introduction, this inhibition of resonance delocalization attenuates the effectiveness of the coupling fragment to high-spin couple unpaired electrons.^{1,9–11}



Structures considered for the spin-protecting group include tertiary alkyl groups and polycyclic (bicyclic or tricyclic) ring systems. Simple primary or secondary alkyl groups are less attractive since they contain allylic hydrogens that are excellent candidates for abstraction and subsequent loss of an unpaired electron (below, left).⁴² Tertiary alkyl spin-protecting groups introduce obvious steric congestion problems (below, center). However, polycyclic ring systems combine the more desirable sterics of a secondary alkyl group with the low chemical reactivity provided by a tertiary alkyl group (below, right). As shown below, the bridgehead hydrogens of a polycyclic spin-protecting group are orthogonal to the TMM π -system and are therefore much less susceptible to abstraction. However, these same hydrogens experience van der Waals repulsions with aryl rings at small torsion angles, as shown below. Thus, biradicals having polycyclic spin-protecting groups are not free from debilitating steric interactions.

Regardless of the structure of the spin-protecting group, this steric interaction could result in reduced exchange coupling. However, polycyclic spin-protecting groups are unique in that the steric interaction can be regulated and should decrease as the bond angle θ decreases, as implied above. Moreover, a gradual change in θ should cause a gradual change in ϕ thereby providing a series of biradicals having incrementally different singlet–triplet gaps. Thus, polycyclic spin-protecting



groups might be superior to tertiary alkyl groups for kinetic protection of the unpaired electrons in TMM-type biradicals and should be a particularly useful structural element for studying the effect of bond torsion on exchange coupling in TMM-type biradicals.

To continue exploring this structure–property relationship, the TMM-type dinitroxides in this study are designed to have a range of aryl torsion angles: large torsions ($>60^\circ$, $2^{\bullet\bullet}, 5^{\bullet\bullet}$), moderate torsions ($\approx 60^\circ$, $1^{\bullet\bullet}, 4^{\bullet\bullet}$), small torsions ($<60^\circ$, $3^{\bullet\bullet}$), and no aryl torsions ($7^{\bullet\bullet}$). Of course the *tert*-butylnitroxide groups in these dinitroxides are free to rotate and assume any torsion angles, but this torsional motion should not be coupled to the structure of the spin-protecting group. Introduction of structural elements to prohibit rotation of the *tert*-butylnitroxide groups, analogous to those that prohibit phenyl torsions in biradical $7^{\bullet\bullet}$, is more challenging to implement synthetically. Moreover, unless there are substituents ortho to the *tert*-butylnitroxide group, it usually adopts a conformation having little torsion with respect to the phenyl group, as shown in crystal structures of several nitroxides and their complexes.⁴³ That is, *tert*-butylnitroxide torsion is typically less than aryl group torsions in 1,1-diarylethenes, and more importantly there is no reason to expect that *tert*-butylnitroxide torsion will vary in our series of dinitroxides. Nonetheless, *tert*-butylnitroxide torsion is as important as aryl torsion, but we cannot deconvolute the two torsions in the present study. Studies of exchange coupling in the solid state in conjunction with molecular structures determined by X-ray crystallography are needed to deconvolute the effects of the two torsions. Efforts along these lines will be the subject of future reports. Dinitroxide $7^{\bullet\bullet}$ should combine the best of both worlds: a planar TMM-type coupler (no phenyl torsions) having steric protection near *both* the aryl ring and the ethene coupler fragment.

Biradical $6^{\bullet\bullet}$ has phenyl-*tert*-butylnitroxide groups arranged in a *geminal* fashion, as in the TMM-type biradicals, but joined to an sp^3 -hybridized carbon and is therefore geometrically similar to $1^{\bullet\bullet}$ – $5^{\bullet\bullet}$. This is not to say that there is no through-bond coupling in $6^{\bullet\bullet}$, rather that the through-space interaction of the radical halves of $6^{\bullet\bullet}$ are similar to those in $1^{\bullet\bullet}$ – $5^{\bullet\bullet}$, and that the coupling is not regulated by a π -bond. Thus, $6^{\bullet\bullet}$ is a model compound, and comparison of its properties to those of the TMM-type dinitroxides serves as a check of the utility of the ethene coupler of the latter. Our studies of TMM-type bis(semiquinone)s included a model biradical analogous to $6^{\bullet\bullet}$ (having a fluorenyl coupler) that promoted

(43) Aryl-*tert*-butylnitroxide torsion angles in the following citations vary from ca. 2° to ca. 38° : Kitano, M.; Ishimaru, Y.; Inoue, K.; Koga, N.; Iwamura, H. *Inorg. Chem.* **1994**, *33*, 6012; Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1993**, *97*, 13267; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 927; Nakazono, S.; Karasawa, S.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1550.

(42) Anderson, K. K.; Shultz, D. A.; Dougherty, D. A. *J. Org. Chem.* **1997**, *62*, 7575.

antiferromagnetic coupling in opposition to the TMM couplers studied.⁴⁴

Molecular Mechanics Calculations. The results of the MM2 calculations on the model compounds in Figure 2 clearly indicate an increase in phenyl torsion as the valence angle increases from diphenylmethylenenorbornane to diphenylmethylenadamantane to diphenylmethylenebicyclo[4.4.1]undecane, supporting our hypothesis concerning the relationship between θ and ϕ .¹¹ The results of the calculations were also useful in comparing the geometries of bicyclic/tricyclic spin-protecting groups with the noncyclic spin-protecting groups. Thus, *i*-propyldiphenylmethane is sterically similar to diphenylmethylenadamantane, while 1,1-diphenyl-2,2-di-*tert*-butylethene is similar to diphenylmethylenebicyclo[4.4.1]undecane. This illustrates the impact of the bridgehead hydrogen on phenyl torsion in the compounds having bicyclic or tricyclic spin-protecting groups—that is, the bicyclic or tricyclic groups can be sterically demanding substituents due to the orientation of the bridgehead hydrogens.

Fluid Solution EPR Spectroscopy. The N- and H-hfcc do not vary in a regular fashion in either series of biradicals or monoradicals and are therefore not an indicator of any differences in conformation as hfcc of substituted biphenylnitroxides were shown to be.⁴⁵

Since the spin-protecting group modulates phenyl torsion angles, one might expect a dependence of torsional dynamics on the structure of the spin-protecting group. The torsional dynamics is expected to manifest itself in EPR spectral shape for the biradicals since torsion affects spin density in the ethene fragment, and therefore torsion modulates the exchange parameter, J . That is, the biradicals might be expected to exhibit J -modulated EPR spectra.^{46–48} However, even though $|J|$ should be rather small due to both (a) bond torsions that limit spin delocalization, and (b) the fact that the phenyl rings for *tert*-butylphenylnitroxides carry spin densities of only ca. 0.1–0.15,^{45,49} the average J might be much greater than in biradicals known to exhibit J -modulation. In addition, the torsional correlation time, τ is expected to be very small.^{2,3} Therefore, we expect the spectral manifestations of J -modulation to be subtle, and indeed we found no evidence for J -modulation.⁵⁰

In addition, the fluid-solution EPR spectral appearance of $7^{\bullet\bullet}$ is temperature-independent. Thus, in a molecule where aryl torsion is precluded, the free to rotate *tert*-butylnitroxide groups have no apparent effect on spectral appearance.

Frozen-Solution EPR Spectroscopy. The calculated D -values illustrate the geometric differences in the series of biradicals in a manner consistent with the results of MM2 calculations on the model compounds in Figure 2.

(44) Shultz, D. A.; Boal, A. K.; Lee, H.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 9462.

(45) Shultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 769.

(46) Luckhurst, G. R. *Mol. Phys.* **1966**, *10*, 543.

(47) Hudson, A.; Luckhurst, G. R. *Chem. Rev.* **1969**, *69*, 191.

(48) Marshall, J. H. *J. Chem. Phys.* **1967**, *47*, 1374–1378.

(49) Aurich, H. G.; Hahn, K.; Stork, K.; Weiss, W. *Tetrahedron* **1977**, *33*, 969.

(50) Simulation of the spectra provided no evidence for differential J -modulation within the series of biradicals. We used a correlation time, τ , of ca. 5 ps, in accord with the reported torsional barrier of 1,1-diphenylethene.^{2,3} Also, the planar dinitroxide, $7^{\bullet\bullet}$, does not behave differently from the other dinitroxides. Thus, the absence of J -modulation is most likely a combination of a large average J , and fast correlation times of the nitroxide groups themselves.

For organic biradicals lacking significant spin–orbit coupling, $|D/hc|$ is inversely proportional to the cube of the average interelectronic separation.^{51,52} As can be seen in Table 2, for the TMM-type biradicals, $D(2^{\bullet\bullet}) > D(5^{\bullet\bullet}) > D(4^{\bullet\bullet}) \approx D(1^{\bullet\bullet}) > D(3^{\bullet\bullet}) \approx D(7^{\bullet\bullet})$ —the same order as decreasing aryl ring torsion angles. Since smaller torsion angles correspond to greater spin delocalization, and therefore greater interelectronic separation, the trend in D supports greater delocalization from $2^{\bullet\bullet} \rightarrow 5^{\bullet\bullet} \rightarrow 4^{\bullet\bullet} \rightarrow 1^{\bullet\bullet} \rightarrow 3^{\bullet\bullet}/7^{\bullet\bullet}$, in good agreement with the MM2-derived geometries of the corresponding hydrocarbons shown in Figure 2. Examination of the bond and torsion angles given in Figure 2 shows that the spatial orientation of the phenyl rings in 9,9-diphenylfluorene most closely matches that of diphenylmethylenenorbornane. The corresponding biradicals, $6^{\bullet\bullet}$ and $3^{\bullet\bullet}$, respectively, have similar D -values. We believe the difference in D -values between $6^{\bullet\bullet}$ and $3^{\bullet\bullet}$ is consistent with $3^{\bullet\bullet}$ having additional delocalization (into the ethene coupler) that is not possible in $6^{\bullet\bullet}$ which has an sp^3 -hybridized coupler. Finally, the D -values for $3^{\bullet\bullet}$ and $7^{\bullet\bullet}$ are nearly equal, but based solely on differences in delocalization, one would expect the D -value for $7^{\bullet\bullet}$ to be less than that of $3^{\bullet\bullet}$. We feel that the similarity of the two values could be a result of the limitation of the method used to estimate D -values.

As seen in Figure 6, the temperature variation of the $\Delta m_s = 2$ transition intensities for $1^{\bullet\bullet}$ – $4^{\bullet\bullet}$, $6^{\bullet\bullet}$, and $7^{\bullet\bullet}$ follow the Curie law from ca. 8 to ca. 50 K, consistent with $J \geq 0$, i.e., consistent with both a triplet ground-state and a singlet–triplet degeneracy.³³ Thus, there is no evidence from the Curie plots of dramatically different exchange couplings as a function of the spin-protecting groups in this series of biradicals. Interestingly, biradical $6^{\bullet\bullet}$, in which the spin-coupling fragment is an sp^3 -hybridized carbon, exhibits a linear Curie plot, unlike its bis-(semiquinone) analogue.⁴⁴ The linearity of the Curie plot is most likely evidence of a very small J -value, although ferromagnetic coupling for biradicals having sp^3 -hybridized couplers is predated.⁶ Dougherty's group presented computational evidence that, as a result of a balance of through-bond and through-space effects, coupling in the 1,3-biradical trimethylene (a biradical with an sp^3 -hybridized coupler) ranges from ferromagnetic to antiferromagnetic depending both on the central bond angle and on terminal methylene torsions.^{35,53} The J -values in trimethylene-type biradicals are ca. 1 order of magnitude smaller than J for biradicals coupled through π -systems.^{6,8} This intrinsically weaker coupling and the fact that the spin density in the phenyl ring of a phenyl-*tert*-butylnitroxide is ca. 0.1–0.15,^{45,49} leads us to suggest that J for $6^{\bullet\bullet}$ is weaker than in the TMM-type biradicals.

Also noteworthy is that biradical $2^{\bullet\bullet}$ exhibits a linear Curie plot despite the fact that di-*tert*-butyl might be expected to exhibit greater steric demand than bicyclo[4.4.1]undecane. We point out that the aryl groups of $2^{\bullet\bullet}$ are capable of “gearing” with the *tert*-butyl groups, whereas in $5^{\bullet\bullet}$ such a conformation is not possible. Geared conformations in $2^{\bullet\bullet}$ should give a range of more positive J -values, hence the linear Curie plot.

Overall, steric bulkiness does manifest itself in exchange coupling of TMM-type dinitroxides. Unlike the

(51) Gleason, W. B.; Barnett, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 2701.

(52) Keana, J. F.; Dinerstein, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2808.

(53) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

Curie plots for **1**^{••}–**4**^{••}, **6**^{••}, and **7**^{••} the Curie plot for **5**^{••}, shown in Figure 7, is characteristic of a low-spin ground-state. A multiparameter fit of the data gives $J = -68 \pm 6$ cal/mol—a rather large negative value considering that $J = +13$ cal/mol for **1**^{••}.¹³ Thus, polycyclic spin-protecting groups can permit greater spin delocalization into the TMM spin coupler (as in **3**^{••}) or they can very effectively inhibit spin delocalization and give rise to a singlet ground state as in **5**^{••}.

Conclusions

Several dinitroxide biradicals have been prepared that differ in *tert*-butylaminoxylphenyl ring torsion angles by virtue of different steric demand of their spin-protecting groups. In addition, the synthesis of a TMM-type dinitroxide having a planar π -system was prepared. The synthetic route employed for the planar TMM-type biradical should be general and should therefore expand the utility of TMM-type biradicals that are susceptible to bond torsions that attenuate exchange coupling. These dinitroxides are designed to be an effective series of molecules to map out J -coupling/conformation space in TMM-type biradicals.

Molecular mechanics was used to estimate the differences in phenyl torsion in a series of 1,1-diphenylethenes that serve as conformational models for the corresponding dinitroxides. Bicyclic/tricyclic spin-protecting groups can be sterically demanding at large bond angles, θ . Conversely, bicyclic/tricyclic spin-protecting groups having a small bond angle θ allow for greater delocalization in the diphenylethene unit by permitting smaller phenyl torsions, ϕ .

EPR spectroscopic parameters (hfcc and D -values) were examined to determine if their values reflected differences in conformation in the series of biradicals. Interestingly, neither N- nor H-hfcc varied within our series of biradicals/monoradicals in a regular fashion indicating that there is no apparent relationship between N- or H-hfcc and conformation as in biphenyl-*tert*-butylnitroxides.⁴⁵ Also, the biradicals studied do not exhibit J -modulated EPR spectra. However, D -values, estimated from relative intensities of $\Delta m_s = 1$ and $\Delta m_s = 2$ transitions,³² are consistent with a varied degree of delocalization in the dinitroxides: smaller D -values for biradicals having smaller aryl torsions, and larger D -values for dinitroxides having greater aryl torsions.

All the biradicals studied, except **5**^{••}, exhibited linear Curie plots. These results are consistent with both triplet ground-states and singlet–triplet degeneracies. Interestingly, dinitroxide **6**^{••} exhibited a linear Curie plot, despite the lack of a π -coupling fragment. We feel these results indicate that the singlet triplet gaps are probably small, and that of **6**^{••} is smaller than the TMM-type dinitroxides. Indeed, the triplet ground state of **1**^{••} lies only 13 cal/mol below the singlet state,¹³ and so our series of biradicals probably have similar J -values. The notable exception is biradical **5**^{••}, a ground-state singlet species with the triplet lying about 140 cal/mol above the singlet.

In summary, the affect of bond torsions on exchange coupling the series of TMM-type dinitroxides as determined by variable-temperature EPR was manifested only in biradical **5**^{••}, presumably due to large phenyl torsions. Differences in exchange couplings in TMM-type dinitroxides other than **5**^{••} are probably subtle and should be revealed in solid-state magnetic susceptibility experi-

ments. In addition, solid-state studies are needed to separate effects due to phenyl-*tert*-butylnitroxide torsion from aryl torsion. Studies of solid-state structure and properties of **1**^{••}–**7**^{••} are underway.

Experimental Section

Compounds **1**^{••},¹³ **8**,⁴⁴ **9**,⁹ **10**,⁵⁴ and di-*tert*-butyl ketone hydrazone¹⁷ were prepared according to literature procedures. Carbinol **17** was prepared by NaBH₄ reduction of the commercially available 4,4'-dibromobenzophenone (**15**) and used without purification. Di-*tert*-butyldiazomethane was prepared in excellent yield by oxidation of the corresponding hydrazone as described below, in contradiction to an earlier report.¹⁷ Solvent distillations, synthetic procedures, and EPR sample preparation were carried out under an argon or nitrogen atmosphere, often in combination with the use of a glovebox. THF and toluene were distilled from sodium benzophenone–ketyl prior to use. NMR spectra were recorded at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR). Elemental analysis was performed by Atlantic Microlab, Inc, Norcross, GA. X-Band EPR spectroscopy was performed as described previously.⁵⁵ Room-temperature magnetic moments were measured on a Cahn Faraday Balance, calibrated with Hg[Co(SCN)₄].

Nitroxide Chromatography. Following removal of solids from the oxidation reaction, the crude reaction mixture is first chromatographed on a silica gel column using gradient elution (0 to 1% THF/CH₂Cl₂). This column separates mononitroxide from other products. The remaining red material is subjected to a second column again using gradient elution (0 to 25% ether/petroleum ether) to obtain pure dinitroxide. Nitroxides from **1-Br**–**6-Br** were purified by this procedure. All biradicals had room-temperature magnetic moments of 2.6 ± 0.2 Bohr magnetons—consistent with two unpaired electrons.

2-(4-Chloro-*n*-butyl)cycloheptanone, 12. Cycloheptanone (2.85 g, 25.5 mmol) was dissolved in 75 mL of THF in a 250 mL Schlenk flask and cooled to -78 °C. LDA (prepared from the addition of 10.2 mL of a 2.5 M BuLi solution to 2.59 g, 25.5 mmol, *i*-Pr₂NH in 10 mL THF) was then added dropwise, and the reaction was warmed to room temperature followed by recooling to -78 °C. 4-Chloro-1-iodobutane (5.0 g, 22.9 mmol) was then added as a solution in 5 mL of THF, and the reaction was stirred 12 h while warming to room temperature. The reaction was quenched with 1 mL of a 1 M aqueous HCl solution, transferred to a separatory funnel, washed once 1 M aqueous HCl and once with saturated aqueous NaCl, and dried over Na₂SO₄. Following filtration and evaporation, the residue was subjected to chromatography (SiO₂, gradient elution: 0 to 2% ether/petroleum ether) to give the product as a colorless oil (2.32 g, 50%). ¹H NMR (CDCl₃) δ (ppm): 3.52 (t, $J = 6.7$ Hz, 2H), 2.5 (m, 3H), 2.0–1.0 (m, 14H). ¹³C NMR (CDCl₃) δ (ppm): 215.9, 51.0, 44.3, 43.8, 32.6, 31.5, 31.3, 29.5, 32.6, 25.6, 24.5. IR (film from CH₂Cl₂) ν (cm⁻¹): 1700. HRMS (EI) calcd for C₁₁H₁₉ClO (M⁺): 202.1124. Found: 202.1130.

Bicyclo[4.4.1]undecan-11-one, 13. 2-(4'-Chloro-*n*-butyl)-cycloheptanone, **12** (1.44 g, 7.11 mmol), and NaI (5.3 g, 36 mmol) were dissolved in 100 mL of reagent grade acetone in a 250 mL round-bottom flask and refluxed 12 h. Acetone was evaporated and the yellow/brown solid mass partitioned between H₂O and Et₂O. The organic portion was transferred to a separatory funnel, washed once with H₂O and once with saturated aqueous NaCl, and dried over Na₂SO₄. Solvent removal yielded the iodide as a viscous, air-sensitive yellow oil which was used without purification. The crude iodide was dissolved in 40 mL of THF in a 250 mL Schlenk flask and cooled to -78 °C. LiHDMS (prepared from the addition of 3.0 mL of 2.5 M BuLi solution to 1.43 g, 1.25 mmol, (SiMe₃)₂NH in 10 mL of THF) was added dropwise, and the reaction mixture was allowed to warm to room temperature immediately after addition. We found it to be important to add

(54) Davies, D. I.; Hey, D. H.; Summers, B. *J. Chem. Soc. C* **1970**, 2653.

(55) Shultz, D. A.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 6254.

LiHDSMS slowly and warm the reaction immediately after addition in order to maximize yield of the desired ketone. The reaction was stirred 12 h, quenched with 1 mL of a 1 M aqueous HCl solution, transferred to a separatory funnel, washed once 1 M aqueous HCl and once with saturated aqueous NaCl, dried over Na₂SO₄, filtered, and evaporated to dryness. Chromatography (SiO₂, gradient elution: 0 to 10% ether/petroleum ether) gave the product as a colorless oil (770 mg, 65%). ¹H NMR (CDCl₃) δ (ppm): 2.77 (m, 2H), 1.81 (m, 8H), 1.65 (m, 4H), 1.48 (m, 4H). ¹³C NMR (CDCl₃) δ (ppm): 219.3, 34.9, 27.1, 26.4. IR (film from CH₂Cl₂) ν (cm⁻¹): 1690. Anal. Calcd for C₁₁H₁₈O: C, 79.46; H, 10.91. Found; C, 79.33; H, 10.85.

Bicyclo[4.4.1]undecan-11-one Hydrazone. Bicyclo[4.4.1]-undecan-11-one, **13** (1.2 g, 7.25 mmol), hydrazine monohydrate (10 g, 200 mmol, 10 mL), and hydrazine sulfate (1.0 g, 9 mmol) were combined in a 25 mL round-bottom flask. The resulting biphasic mixture was refluxed for 4 days, and upon cooling a solid precipitated. This mixture was transferred to a separatory funnel containing H₂O and Et₂O, washed twice with H₂O and once with saturated brine, and dried over Na₂SO₄. Solvent removal gave a white solid which was used without further purification. ¹H NMR (CDCl₃) δ (ppm): 4.9 (broad s, 2H), 3.13 (m, *J* = 7.6 Hz, 1H), 2.76 (m, *J* = 5.7 Hz, 1H), 1.8–1.1 (m, 16H). ¹³C NMR (CDCl₃) δ (ppm): 162.6, 48.0, 36.3, 30.7, 28.7, 26.6, 26.2. IR (film from CH₂Cl₂) ν (cm⁻¹): 3331, 3216, 1638. HRMS (EI) calcd for C₁₁H₂₀N₂ (M⁺): 180.1626. Found: 180.1630.

11-Diazobicyclo[4.4.1]undecane, 14. Bicyclo[4.4.1]undecan-11-one hydrazone (300 mg, 1.67 mmol) was dissolved in 30 mL of Et₂O and added to yellow HgO (2.0 g, 9.23 mmol). Na₂SO₄ (2.0 g, 14.08 mmol) was added, followed by a few drops of a saturated ethanolic solution of NaOH. The resulting yellow suspension was stirred for 14 h, filtered, and evaporated to yield a crystalline orange solid. The IR spectrum of this material was consistent with nearly complete conversion to the product (no NH stretches at 3331 and 3216 cm⁻¹), and the material was used without further purification. IR (film from CH₂Cl₂) ν (cm⁻¹): 2024.

Di-*tert*-butyldiazomethane. Di-*tert*-butyl ketone hydrazone (490 mg, 3.1 mmol) was dissolved in 30 mL of Et₂O and added to yellow HgO (1.5 g, 6.9 mmol). Na₂SO₄ (2.0 g, 14 mmol) was added, followed by a few drops of a saturated ethanolic solution of NaOH, and the resulting yellow suspension was stirred for 4 h. After this time, the mixture was filtered and evaporated to yield a thick orange liquid. This material was distilled (25 °C, 100 mTorr) with a Kugelrohr apparatus to give the pure diazoalkane, having the signature IR stretch (2027 cm⁻¹) cited in the literature.¹⁶

Adamantylbis(4'-bromophenyl)carbinol. In a 100 mL Schlenk flask, 1,4-dibromobenzene (2.10 g, 8.88 mmol) was dissolved in 20 mL of THF and cooled to -78 °C. *tert*-Butyllithium (11.3 mL of a 1.5 M solution) was added dropwise and the reaction stirred for 1 h at -78 °C, yielding a turbid, colorless solution. Ester **9** (750 mg, 3.86 mmol) was then added as a solution in 10 mL of THF, and the reaction allowed to stir 12 h at ambient temperature. The reaction was quenched with saturated aqueous NH₄Cl (2.5 mL), transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected and dried over Na₂SO₄, filtered, and evaporated to dryness. The residue was subjected to radial chromatography (SiO₂, gradient elution: 1% to 10% Et₂O/petroleum ether) to give the product as a colorless solid (1.57 g, 87%). ¹H NMR (CDCl₃) δ (ppm): 7.41 (d, *J* = 7.5 Hz, 4H), 7.29 (d, *J* = 7.6 Hz, 4H), 2.61 (s, 1H), 2.24–2.20 (broad m, 3H), 1.73–1.92 (broad m, 10H), 1.54–1.59 (broad m, 2H). ¹³C NMR (CDCl₃) δ (ppm): 146.2, 131.4, 127.5, 120.6, 82.5, 49.7, 41.2, 38.4, 33.5, 29.2, 28.6, 27.1. IR (film from CH₂Cl₂) ν (cm⁻¹): 3614. Anal. Calcd for C₂₃H₂₄Br₂O: C, 59.04; H, 4.96. Found; C, 58.81; H, 5.09.

Bis(4'-bromophenyl)methyleneadamantane, 4-Br₂. The carbinol from the previous reaction (1.21 g, 2.56 mmol) and *p*-toluenesulfonic acid hydrate (25 mg) were added to a 250 mL round-bottom flask containing 125 mL of benzene. The flask was connected to a Dean–Stark trap/reflux condenser assembly and refluxed for 3 h with azeotropic removal of water.

The reaction was cooled, transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected, dried over Na₂SO₄, filtered, and evaporated to dryness. The resulting solid was subjected to radial chromatography (SiO₂, petroleum ether) to give the product as a colorless solid (1.12 g, 96%). ¹H NMR (CDCl₃) δ (ppm): 7.39 (d, *J* = 8.1 Hz, 4H), 6.97 (d, *J* = 7.9 Hz, 4H), 2.73 (broad s, 2H), 7.99 (broad m, 2H), 1.85 (broad m, 10H). ¹³C NMR (CDCl₃) δ (ppm): 148.4, 141.3, 131.3, 128.5, 120.3, 39.6, 37.0, 34.6, 28.1. Anal. Calcd for C₂₃H₂₂Br₂: C, 60.28; H, 4.83. Found; C, 60.35; H, 4.85.

Bis(4'-*tert*-butylaminoxylphenyl)methyleneadamantane, 4" (and 4'). 4-Br₂ (500 mg, 1.09 mmol) was dissolved in 20 mL of THF in a 100 mL Schlenk flask and cooled to -78 °C. *tert*-Butyllithium (2.91 mL of a 1.5 M solution) was then added dropwise, and the resulting pink to light red solution was stirred for 3 h at -78 °C. A solution of 2-methyl-2-nitrosopropane dimer (210 mg, 1.20 mmol) was then added as a solution in 15 mL of THF and the reaction stirred 12 h. The resulting emerald green solution was quenched with NH₄Cl (3 mL), transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected and dried over Na₂SO₄. When the solvent was removed, either a viscous oil or solid remained, and the product was often slightly colored due to aerial oxidation of the hydroxylamine. The resulting material was oxidized without purification by stirring with AgO (1.5 g, 12.1 mmol) in 15 mL of THF for 3 h under argon and protected from light. The resulting deep red solution was filtered through Celite and the solvent removed to give a dark red solid. This solid was chromatographed to give monoradical (107 mg, 26%) and 4" (272 mg, 53%). Monoradical: HRMS (FAB) calcd for C₂₇H₃₃NO (M⁺ + H): 387.2562. Found: 387.2569. 4": HRMS (FAB) calcd for C₃₁H₄₂N₂O₂ (M⁺ + 2H): 474.3246. Found: 474.3260.

Norbornylbis(4'-bromophenyl)carbinol. In a 100 mL Schlenk flask, 1,4-dibromobenzene (1.76 g, 7.47 mmol) was dissolved in 20 mL of THF and cooled to -78 °C. *tert*-Butyllithium (9.53 mL of a 1.5 M solution) was then added dropwise and the reaction stirred for 1 h at -78 °C, yielding a turbid, colorless solution. Ester **8** (500 mg, 3.25 mmol) was then added as a solution in 10 mL of THF, and the reaction allowed to stir 12 h at ambient temperature. The reaction was quenched with saturated aqueous NH₄Cl (2.5 mL), transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected and dried over Na₂SO₄, filtered, and evaporated to dryness. The residue was purified by radial chromatography (SiO₂, gradient elution: 1% to 10% Et₂O/petroleum ether) to give the product as a colorless solid (1.21 g, 85%). ¹H NMR (CDCl₃) δ (ppm): 7.42 (d, *J* = 8.8 Hz, 4H), 7.28 (d, *J* = 8.7 Hz, 4H), 2.41 (broad s, 1H), 1.97 (broad m, 3H), 1.66 (broad m, 4H), 1.18–1.26 (broad m, 6H). ¹³C NMR (CDCl₃) δ (ppm): 147.0, 131.2, 127.9, 120.6, 78.5, 57.5, 38.1, 31.2, 30.0. IR (film from CH₂Cl₂) ν (cm⁻¹): 3586. Anal. Calcd for C₂₀H₂₀Br₂O: C, 55.07; H, 4.62. Found: C, 54.99; H, 4.71.

Bis(4'-bromophenyl)methylenenorbornane, 3-Br₂. The carbinol from the previous reaction (1.0 g, 2.29 mmol) and *p*-toluenesulfonic acid hydrate (25 mg) were added to a 250 mL round-bottom flask with 125 mL of benzene. A Dean–Stark trap/reflux condenser assembly was attached to the flask, and the reaction mixture was refluxed for 3 h. The solution was cooled, transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was dried over Na₂SO₄, filtered, and evaporated to dryness. The resulting solid was purified by radial chromatography (SiO₂, petroleum ether) to give the product as a colorless solid (910 mg, 95%). ¹H NMR (CDCl₃) δ (ppm): 7.39 (d, *J* = 8.6 Hz, 4H), 6.98 (d, *J* = 8.5 Hz, 4H), 2.63 (broad m, 2H), 1.73 (broad m, 4H), 1.44 (broad m, 4H). ¹³C NMR (CDCl₃) δ (ppm): 152.0, 141.3, 131.5, 131.1, 124.5, 120.6, 38.2, 28.9. Anal. Calcd for C₂₀H₁₈Br₂: C, 57.45; H, 4.34. Found; C, 57.55; H, 4.41.

Bis(4'-*tert*-butylaminoxylphenyl)methylenenorbornane, 3" (and 3'). 3-Br₂ (500 mg, 1.12 mmol) was dissolved in 20 mL of THF in a 100 mL Schlenk flask and

cooled to -78°C . *tert*-Butyllithium (3.12 mL of a 1.5 M solution) was then added dropwise and the resulting solution stirred for 3 h at -78°C . A solution of 2-methyl-2-nitrosopropane dimer (230 mg, 1.3 mmol) was then added as a solution in 15 mL of THF and the reaction stirred 12 h. The resulting solution was quenched with NH_4Cl (3 mL), transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected and dried over Na_2SO_4 . When the solvent was removed, either a viscous oil or solid remained, and the product was often slightly colored due to aerial oxidation of the hydroxylamine. The resulting material was oxidized without purification by stirring with AgO (1.5 g, 12.1 mmol) in 15 mL of THF for 3 h under argon and protected from light. The resulting deep red solution was filtered through Celite and the solvent removed to give a dark red solid which was chromatographed to give monoradical (78 mg, 19%) and **3 $\cdot\cdot$** (326 mg, 63%). Monoradical: HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{29}\text{NO}$ ($\text{M}^+ + \text{H}$): 347.2249. Found: 347.2240. **3 $\cdot\cdot$** : HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{38}\text{N}_2\text{O}_2$ ($\text{M}^+ + 2\text{H}$): 434.2933. Found: 434.2928.

9,9-Bis(4'-bromophenyl)fluorene, 6-Br $_2$. A 100 mL Schlenk flask was charged with 1,4-dibromobenzene (2.41 g, 9.43 mmol). This material was dissolved in 15 mL of THF and cooled to -78°C , *tert*-butyllithium (12.6 mL of a 1.5 M solution) was then added dropwise, and the resulting turbid white solution was stirred for 1 h at -78°C . Methyl 2-phenylbenzoate, **10** (1.0 g, 4.71 mmol), in 5 mL of THF was then added, and the reaction was allowed to stir at room temperature 12 h. The reaction was quenched with 1 mL of a saturated NaCl solution, transferred to a separatory funnel, washed with a saturated NaCl solution, dried over MgSO_4 , filtered, and evaporated to dryness. The crude product was added to a 25 mL beaker containing poly[phosphoric acid] (10 g) and heated to 80°C for 10 min during which time the brown solution produced a white precipitate. This mixture was then cooled and quenched with crushed ice, poured into a separatory funnel, and extracted with Et_2O . The organic solution was washed once with a saturated NaCl solution, filtered, dried over MgSO_4 , and evaporated to dryness. The resulting material was purified by radial chromatography (SiO_2 , petroleum ether) to give the product as a colorless solid (220 mg, 92%). ^1H NMR (CD_2Cl_2) δ (ppm): 7.80 (d, $J = 7.5$ Hz, 2H), 7.36 (m, 10H), 7.06 (d, $J = 8.6$ Hz, 4H). ^{13}C NMR (CDCl_3) δ (ppm): 150.13, 144.50, 140.04, 131.42, 129.75, 127.96, 127.90, 120.92, 120.39, 64.58. Anal. Calcd for $\text{C}_{25}\text{H}_{16}\text{Br}_2$: C, 63.06; H, 3.39. Found: C, 63.18; H, 3.44.

9,9-Bis(4'-tert-butylaminoxylphenyl)fluorene, 6 $\cdot\cdot$ (and 6 \cdot), 6-Br $_2$ (500 mg, 1.05 mmol) was dissolved in 20 mL of THF in a 100 mL Schlenk flask and cooled to -78°C . *tert*-Butyllithium (2.8 mL of a 1.5 M solution) was then added dropwise and the resulting pink to light red solution stirred for 3 h at -78°C . A solution of 2-methyl-2-nitrosopropane dimer (200 mg, 1.3 mmol) was then added as a solution in 15 mL of THF and the reaction stirred 12 h. The resulting emerald green solution was quenched with NH_4Cl (3 mL), transferred to a separatory funnel, and washed once with saturated aqueous NaCl. The organic portion was collected and dried over Na_2SO_4 . When the solvent was removed, either a viscous oil or solid remained, and the product was often slightly colored due to aerial oxidation of the hydroxylamine. The resulting material was oxidized without purification by stirring with AgO (1.5 g, 12.1 mmol) in 15 mL of THF for 3 h under argon and protected from light. The resulting deep red solution was filtered through Celite and the solvent removed to give a dark red solid which was chromatographed to give mononitroxide (320 mg, 40%) and dinitroxide, **6 $\cdot\cdot$** (270 mg, 33%). Mononitroxide: HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{27}\text{NO}$ ($\text{M}^+ + \text{H}$): 405.2093. Found: 405.2087. **6 $\cdot\cdot$** : HRMS (FAB) calcd for $\text{C}_{33}\text{H}_{36}\text{N}_2\text{O}_2$ ($\text{M}^+ + 2\text{H}$): 492.2777. Found: 492.2751.

4,4'-Dibromothiobenzophenone, 16. 4,4'-Dibromobenzophenone (2.0 g, 6.03 mmol) and P_4S_{10} (4.02 g, 9.05 mmol) were suspended in 20 mL of acetonitrile. NaHCO_3 (3.1 g, 36 mmol) was then added and the mixture heated to 50°C . The resulting mixture was then allowed to stir 12 h, during which time it became dark blue. After cooling, the mixture was

transferred to a separatory funnel containing Et_2O and H_2O , and the resulting blue organic layer was washed three times with saturated aqueous NaHCO_3 , washed once with saturated aqueous NaCl, and then dried over Na_2SO_4 . The solvents were removed to give a blue solid which was recrystallized (argon was blown over the solution during boiling and cooling) from MeOH to give dark blue microcrystals of the product. This material was contaminated (ca. 25% by ^1H NMR) with starting material; however, the subsequent reaction was unaffected by this, so no further purification was attempted.

Bis(4',4''-bromophenyl)methylenebicyclo[4.4.1]-undecane Episulfide. Thioketone **16** (ca. 1.14 g, ca. 3.25 mmol) was dissolved in 5 mL of THF in a 50 mL round-bottom flask to give a deep blue solution. Diazoalkane **14** (580 mg, 3.25 mmol) was then added as an orange solution in 15 mL of THF, causing gas evolution, and the resulting blue solution protected from light and refluxed 12 h. THF was removed, and the material was subjected to radial chromatography (SiO_2 , petroleum ether) to give the episulfide as a colorless solid (1.06 g, 66%). ^1H NMR (CDCl_3) δ (ppm): 7.50 (d, $J = 8.7$ Hz, 4H), 7.39 (d, $J = 8.6$ Hz, 4H), 2.07 (pent, $J = 6.6$ Hz, 2H), 1.26–1.92 (broad m, 18H). ^{13}C NMR (CDCl_3) δ (ppm): 140.7, 132.6, 130.7, 120.9, 69.1, 66.6, 43.0, 33.9, 31.1, 26.6, 25.4. HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{26}\text{Br}_2\text{S}$ (M^+): 504.0122. Found: 504.0125.

Bis(4'-bromophenyl)methylenebicyclo[4.4.1]-undecane, 5-Br $_2$. The episulfide from the previous reaction (1.06 g, 2.13 mmol) and triphenylphosphine (1.12 g, 4.26 mmol) were dissolved in 15 mL of toluene, and the resulting solution was refluxed for two nights. After cooling, the reaction mixture was filtered through SiO_2 , evaporated, and the residue was subjected to radial chromatography (SiO_2 , petroleum ether) to give the product as a colorless solid (815 mg, 87%). ^1H NMR (CDCl_3) δ (ppm): 7.40 (d, $J = 8.4$ Hz, 4H), 7.07 (d, $J = 8.3$ Hz, 4H), 2.95 (pent, $J = 5.8$ Hz, 2H), 1.5 (broad m, 16H). ^{13}C NMR (CDCl_3) δ (ppm): 148.4, 142.9, 136.7, 131.7, 130.5, 120.1, 41.2, 32.2, 27.0. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{Br}_2$: C, 60.78; H, 5.52. Found: C, 60.54; H, 5.52.

Bis(4'-tert-butylaminoxylphenyl)methylenebicyclo[4.4.1]undecane, 5 $\cdot\cdot$ (and 5 \cdot), 5-Br $_2$ (200 mg, 0.43 mmol) was dissolved in 10 mL of THF in a 50 mL Schlenk flask and cooled to -78°C . *tert*-Butyllithium (1.15 mL of a 1.5 M solution, 1.72 mmol) was then added dropwise and the resulting solution stirred for 3 h at -78°C . 2-Methyl-2-nitrosopropane dimer (83 mg, 0.47 mmol) was then added as a solution in 5 mL of THF, the cooling bath was removed, and the reaction mixture was allowed to stir for 12 h at room temperature. Saturated aqueous NH_4Cl solution (1 mL) was added to quench the reaction, and the mixture was transferred to a separatory funnel, washed once with both saturated aqueous NH_4Cl and saturated aqueous NaCl, separated, filtered, and dried over Na_2SO_4 . Following evaporation, the resulting crude bis(hydroxylamine) was oxidized without purification by stirring over AgO (1.5 g, 12.1 mmol) in 15 mL of THF for 3 h under argon and protected from light. The resulting red suspension was filtered through Celite and the solvent removed to give the crude biradical as a dark red solid. This solid was chromatographed in the usual manner, yielding monoradical (19 mg, 10%) and **5 $\cdot\cdot$** (148 mg, 72%). Monoradical: HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{37}\text{NO}$ ($\text{M}^+ + \text{H}$): 403.2875. Found: 403.2888. **5 $\cdot\cdot$** : HRMS (FAB) calcd for $\text{C}_{32}\text{H}_{46}\text{N}_2\text{O}_2$ ($\text{M}^+ + 2\text{H}$): 490.3559. Found: 490.3548.

Bis(4'-bromophenyl)methylenedi-tert-butylmethane Episulfide. Thioketone **16** (1.02 g, 2.92 mmol) was dissolved in 5 mL of THF in a 50 mL round-bottom flask to give a deep blue solution. Di-*tert*-butyldiazomethane (450 mg, 2.92 mmol) was then added as an orange solution in 15 mL of THF, at which point the color dissipated. The resulting solution, protected from light, was refluxed for 12 h during which time some of the blue color returned. THF was removed, and the material was subjected to radial chromatography (SiO_2 , 5% Et_2O /petroleum ether) to give the episulfide as a light yellow solid (770 mg, 56%). ^1H NMR (d_6 -acetone) δ (ppm): 8.29 (dd, $J = 8.4, 2.3$ Hz, 2H), 7.8 (m, 6H), 1.6 (s, 18H). ^{13}C NMR (CDCl_3) δ (ppm): 145.2, 132.1, 131.8, 131.3, 130.2, 120.3, 76.7, 70.5,

42.0, 34.3. HRMS (FAB) calcd for $C_{22}H_{26}Br_2S$ (M^+): 480.0122. Found: 480.0117.

1,1-Bis(4'-bromophenyl)-2,2-di-*tert*-butylethene, 2-Br₂. The episulfide from the previous reaction (770 mg, 1.62 mmol) and triphenylphosphine (850 mg, 3.24 mmol) were dissolved in 15 mL of toluene, and the resulting solution was refluxed for 48 h. After cooling, the reaction mixture was filtered through SiO_2 and evaporated, and the residue was subjected to radial chromatography (SiO_2 , petroleum ether) to give the alkene as a colorless solid (590 mg, 82%). 1H NMR ($CDCl_3$) δ (ppm): 7.31 (d, $J = 8.5$ Hz, 4H), 6.84 (d, $J = 8.4$ Hz, 4H), 1.56 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 156.0, 148.0, 141.7, 132.0, 130.8, 120.2, 40.5, 35.4. Anal. Calcd for $C_{22}H_{26}Br_2$: C, 58.69; H, 5.82. Found: C, 58.57; H, 5.86.

1,1-Bis(4'-*tert*-butylaminoxylphenyl)-2,2-di-*tert*-butylethene, 2^{••} (and 2[•]). 2-Br₂ (200 mg, 0.45 mmol) was dissolved in 10 mL of THF in a 50 mL Schlenk flask and cooled to -78 °C. *tert*-Butyllithium (1.2 mL of a 1.5 M solution, 1.8 mmol) was then added dropwise and the resulting solution stirred for 3 h at -78 °C. 2-Methyl-2-nitrosopropane dimer (88 mg, 0.50 mmol) was then added as a solution in 5 mL of THF. The cooling bath was removed, and the reaction mixture was stirred for 12 h. Saturated aqueous NH_4Cl solution (1 mL) was added to quench the reaction, and the mixture was transferred to a separatory funnel. The organic layer was washed once with both saturated aqueous NH_4Cl and saturated aqueous NaCl, separated, dried over Na_2SO_4 , filtered, and evaporated. The resulting material was oxidized without purification by stirring with AgO (1.5 g, 12.1 mmol) in 15 mL of THF for 3 h under argon and protected from light. The resulting red suspension was filtered through Celite and the solvent removed to give the crude biradical as a dark red solid. This solid was chromatographed in the usual manner, yielding mononitroxide (17 mg, 8%) and 2^{••} (100 mg, 50%). Monoradical: HRMS (FAB) calcd for $C_{26}H_{37}NO$ ($M^+ + H$): 379.2875. Found: 379.2898. 2^{••}: HRMS (FAB) calcd for $C_{30}H_{46}N_2O_2$ ($M^+ + 2H$): 466.3559. Found: 466.3589.

3-Acetyl-4,4-bis(4'-bromophenyl)butan-2-one. In the glovebox, carbinol **17** (1.98 g, 5.80 mmol), 2,4-pentadione (1.2 mL, 11.59 mmol), and anhydrous $CoCl_2$ (300 mg, 2.32 mmol) were added to a 25 mL Schlenk flask. After a condenser was attached, the flask was removed from the glovebox, connected to a Schlenk line, and heated to reflux for 1 h. The reaction mixture was then cooled to room temperature, CH_2Cl_2 was added, and the mixture was filtered to remove inorganic salts. Solvent was removed by rotary evaporation and the residue was rinsed with petroleum ether. The resulting solid was recrystallized from ethanol to give the product as white needle crystals (2.31 g, 94%). 1H NMR ($CDCl_3$) δ (ppm): 7.40 (d, $J = 8.2$ Hz, 4H) 7.10 (d, $J = 8.2$ Hz, 4H), 4.76 (d, $J = 12.2$ Hz, 1H), 4.63 (d, $J = 12.2$ Hz, 1H), 2.01 (s, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 202.0, 139.8, 132.2, 129.4, 121.3, 74.3, 49.8, 29.6. IR (film from CH_2Cl_2) ν (cm^{-1}): 1736, 1698. Anal. Calcd for $C_{18}H_{16}O_2Br_2$: C, 50.97; H, 3.80. Found: C, 51.08; H, 3.80.

3-Acetyl-4,4-bis(4'-bromophenyl)-3-buten-2-one, 18. A 100 mL Schlenk flask containing 3-acetyl-4,4-bis(4'-bromophenyl)butan-2-one (2.17 g, 5.13 mmol), benzoyl peroxide (372 mg, 1.54 mmol), K_2CO_3 (1.06 g, 7.69 mmol), NBS (912 mg, 5.13 mmol), and 48 mL of CCl_4 was heated to 78 °C for 10–15 min, during which time reaction progress was monitored by TLC. When the reaction was judged complete, and after cooling the reaction mixture, saturated brine was added and the organic layer was separated and evaporated to dryness. The crude product was purified by column chromatography (SiO_2 , 2% ether/petroleum ether) and then crystallized from ether to give **18** as white crystals (1.36 g, 63%). 1H NMR ($CDCl_3$) δ (ppm): 7.51 (d, $J = 8.4$ Hz, 4H) 7.04 (d, $J = 8.4$ Hz, 4H), 1.99 (s, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 202.6, 146.0, 143.9, 137.7, 132.1, 131.5, 31.3. IR (film from CH_2Cl_2) ν (cm^{-1}): 1697, 1667. Anal. Calcd for $C_{18}H_{14}O_2Br_2$: C, 51.21; H, 3.34. Found: C, 51.21; H, 3.38.

5,10-Dibromo-3,12-dihydro-3,3,12,12-tetramethylindeno[1,2-*a*]indene, 7-Br₂. A 50 mL Schlenk flask containing $ZrCl_4$ (893 mg, 3.83 mmol) and a stir bar was prepared in the

glovebox. Freshly distilled THF (9 mL) was added, and after removal from the glovebox, the mixture was cooled to -20 °C. An aliquot of 1.4 M methyllithium (10.4 mL, 14.60 mmol) was added via syringe, and the reaction mixture was stirred for 1 h at -20 °C and 10 min at 25 °C. Dione **18** (770 mg, 1.82 mmol) as a solution in THF (9 mL) was added by cannulation, keeping the temperature at -20 °C. The reaction mixture was stirred for 10 min, after which time the reaction was judged complete by TLC, and quenched by pouring into saturated aqueous brine. The resulting mixture was extracted with ether (3 \times), and the extracts were combined and dried over Na_2SO_4 . After decanting and removing the solvent, the crude product was rinsed with CH_2Cl_2 to give the intermediate diol as a white solid (597 mg, 72%). The diol decomposes (to produce an alkene) in solution at a rate that precludes recording a ^{13}C NMR spectrum. 1H NMR ($CDCl_3$) δ (ppm): 7.37 (d, $J = 8.2$ Hz, 4H) 6.98 (d, $J = 8.2$ Hz, 4H), 3.70 (s, 2H), 1.33 (s, 12H). IR (film from CH_2Cl_2) ν (cm^{-1}): 3270. Anal. Calcd for $C_{20}H_{22}O_2Br_2$: C, 52.88; H, 4.88. Found: C, 52.88; H, 4.91.

A 100 mL round-bottom flask containing the diol from the previous reaction (500 mg, 1.1 mmol) and excess poly[phosphoric acid] (10 g) was heated to 147 °C for ca. 1 h. When judged complete by TLC, the reaction was cooled and carefully poured onto water/crushed ice with stirring. The resulting mixture was extracted with ether (3 \times), and the combined organic extracts were dried with Na_2SO_4 , filtered, and evaporated to dryness. The residue was crystallized from ether to give **7-Br₂** as long, white needles (431 mg, 63%). 1H NMR ($CDCl_3$) δ (ppm): 7.48 (s, 2H) 7.44 (m, 4H), 1.50 (s, 12H). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5, 160.5, 139.7, 135.4, 129.6, 125.2, 120.9, 119.3, 48.1, 24.7. Anal. Calcd for $C_{20}H_{18}Br_2$: C, 57.44; H, 4.33. Found: C, 57.45; H, 4.35.

5,10-Di(tert-butylaminoxyl)-3,12-dihydro-3,3,12,12-tetramethylindeno[1,2-*a*]indene, 7^{••} (and 7[•]). To a solution of **7-Br₂** (275 mg, 0.66 mmol) in THF (14 mL) at -78 °C in a 100 mL Schlenk flask was added *tert*-butyllithium (1.5 M in pentane, 1.77 mL, 2.66 mmol, 4.05 equiv) slowly via syringe. After 4 h at -78 °C, a solution of 2-methyl-2-nitrosopropane dimer (126 mg, 0.72 mmol, 1.1 equiv) in THF (10 mL) was added by cannulation. After stirring 12 h, the reaction was quenched with saturated aqueous NH_4Cl . The resulting mixture was diluted with ether and washed with saturated aqueous NaCl. The organic layer was dried with Na_2SO_4 , filtered, and concentrated under reduced pressure to give the bis(hydroxylamine) as a light yellow solid (285 mg, 99%). IR (film from CH_2Cl_2) ν (cm^{-1}): 3348, 3177.

A mixture of the bis(hydroxylamine) (91.5 mg, 0.211 mmol) and excess AgO (300 mg, 2.42 mmol) in THF (5 mL) was stirred for 4 h. The reaction mixture was passed through a plug of Celite and rinsed with ether. After evaporation, the residue was purified by radial chromatography (SiO_2 , gradient elution: 10% to 30% ether/petroleum ether) to give biradical 7^{••} as a purple solid (67 mg, 73%), and monoradical 7[•] (3.5 mg, 5%). UV-Vis (CH_2Cl_2) λ_{max} (log ϵ): 230 (4.53), 290 (4.39), 349 (4.75), 520 (3.11), 620 (2.94). Monoradical: HRMS (FAB) calcd for $C_{24}H_{29}NO$ ($M^+ + H$): 347.2249. Found: 347.2263. 7^{••}: HRMS (FAB) calcd for $C_{28}H_{38}N_2O_2$ ($M^+ + 2H$): 434.2933. Found: 434.2933.

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Supporting Information Available: Spectral data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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