of ~90 mV suggests that the immobilized electroactive centers do not interact.[9a] The decrease in charging current at the foot of the wave (compare with Figure 9) on addition of $n$-$C_5H_{11}SH$ suggests a more tightly packed film and less anion penetration in the presence of the alkane thiol. The peak current varied linearly with scan rate up to ~2.0 V $s^{-1}$, (Figure 13 insert) and then deviated from linearity at faster scan rates (Figure 13); compare to films of neat [**2**]**6**, where linearity was found up to 50 V $s^{-1}$. Similar results were obtained for mixed films of [**2**]**6** and $n$-$C_{10}H_{21}SH$. These results can be understood in terms of heterogeneous electron transfer rate limitations between the electrode and Ru-group becoming important at high scan rates in the mixed films. Thus if the alkyl thiols chemisorb preferentially on the gold substrate to form a first monolayer film onto which the Ru-staffane complex then adsorbs, the Ru-group would be spaced further from the electrode surface. Under these conditions, electron exchange between the immobilized complex and the substrate in the layered structure will be hampered by the insulating alkyl thiol layer.

The coadsorbed [*n*]**6** exchanged with pure RSH when an electrode first coated with [*n*]**6** was exposed to a solution of the latter. After being exposed to 0.1 mM $C_5H_{11}SH$ in MeCN for 48 h, the cyclic voltammogram of the same electrode showed a peak current ~$10^6$ times smaller than that in the unexchanged voltammogram.

## Conclusions

Self-assembled films of the rigid-rod dithiols [*n*]**4** on gold are disordered, presumably because some of the rods lie and some stand on the surface. They have poor electrode blocking properties. In contrast, self-assembled films of the rigid-rod thiol-thiol acetates [*n*]**5** and ruthenium complexes [*n*]**6** are highly ordered, with the rods perpendicular to the surface, and have excellent blocking properties. Hydrolysis removes the surface acetyl groups from the outer surface of the film assembled from [*n*]**5** without detectable damage to the film or change in the orientation of the rods, and subsequent functionalization with ruthenium pentaammine is possible. The resulting electroactive film has electrochemical properties identical to those of the film self-assembled from [*n*]**6** but has a lower density of the supporting rods. The electrochemical properties of the ruthenated films depend on the pH and on the nature of the supporting electrolyte.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant DMR 8807701 and CHE 8901450), the Robert A. Welch Foundation (Grant 1068), and the Texas Advanced Technology Program. Helpful discussions with Drs. C. Chidsey, H. O. Finklea, and T. Mallouk are acknowledged. We also thank Drs. Chidsey (ref 23e) and Creager (ref 19) for making preprints available to us. We thank Mr. Mark Arendt for preparing the polycrystalline gold electrodes.

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# Intramolecular Magnetic Coupling between Two Nitrene or Two Nitroxide Units through 1,1-Diphenylethylene Chromophores. Isomeric Dinitrenes and Dinitroxides Related in Connectivity to Trimethylenemethane, Tetramethyleneethane, and Pentamethylenepropane

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**Abstract:** Isomeric vinylidenebis(phenylnitrenes) (N) and 1,1-bis[(*N*-oxy-*tert*-butylamino)phenyl]-2-methylpropenes (O) have been prepared, and their EPR fine structures and/or effective magnetic moments have been determined over a wide temperature range. The data were analyzed in terms of Bleaney-Bowers-type equations to give the energy gaps between the quintet and singlet states for N and the triplet and singlet states for O. They were ≫0 $cm^{-1}$, -42.0 $cm^{-1}$ (-502 J/mol, a negative value representing a singlet ground state), and -26.2 $cm^{-1}$ (-313 J/mol), and 10.6 $cm^{-1}$ (127 J/mol), -1.8 $cm^{-1}$ (-22 J/mol), and -3.4 $cm^{-1}$ (-41 J/mol) for *p,p'*-, *m,p'*- and *m,m'*-dinitrenes N and dinitroxides O, respectively. A consistent reduction in the effective intramolecular exchange integrals $J$'s between the two open-shell centers in the latter series is ascribed to the lower spin polarization on the phenyl rings of the dinitroxides relative to the dinitrenes. Whereas the ferro- and antiferromagnetic couplings in the *p,p'* and *m,p'*-topology are consistent not only with the Ovchinnikov's but also Borden-Davidson's rules, the antiferromagnetic interaction in the *m,m'*-substitution pattern is contradictory to the former and consistent with the latter theory. Since the *p,p'*, *m,p'*, and *m,m'* isomers are related to trimethylenemethane (**4**), tetramethyleneethane (**5**), and pentamethylenepropane (**6**), respectively, the results obtained in this work are consistent with the triplet ground state of **4**. **5** and **6** are suggested to have ground singlet states. Radical centers X should be all at the para position for designing super-high-spin polyacetylenes **1** and polydiacetylenes **2**.

As a part of our efforts to design and construct new organic polymers in high-spin ground states,[1] we became interested in knowing if poly(phenylacetylenes) **1** and poly(phenyldiacetylenes) **2** carrying free radical centers X as pendants on the phenyl rings would be high-spin and how strong the electron spins in X could couple each other in the polymer molecules. Experimental results on such polymers so far reported are unsatisfactory or only partly successful[2] in contrast to well-characterized high-spin ground states

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

(2) Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromolecules* **1991**, *24*, 1077. Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 9803. Nishide, H.; Yoshioka, N.; Inagaki, K.; Tsuchida, E. *Macromolecules* **1988**, *21*, 3119. Nishide, H.; Yoshioka, N.; Kaneko, T.; Tsuchida, E. *Macromolecules* **1990**, *23*, 4487. Yoshioka, N.; Nishide, H.; Tsuchida, E. *Mol. Cryst. Liq. Cryst.* **1990**, *190*, 45.

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Chart I

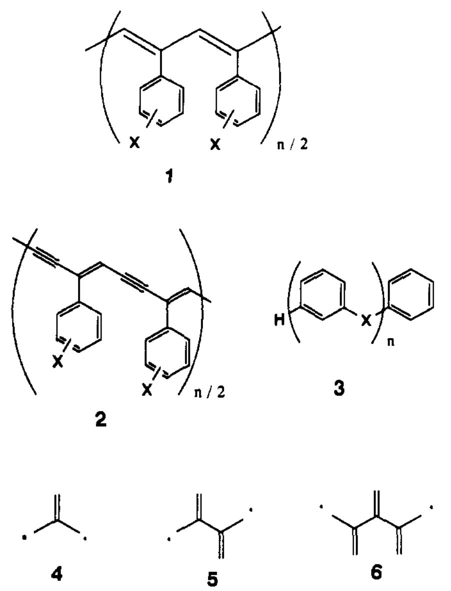
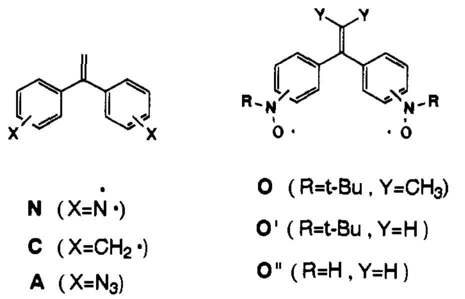


Chart II



of poly($m$-phenylene X)s **3**.[3] In order to answer the above questions, studies of dimeric prototypes as parenthesized in **1** and **2** should be very instructive. We therefore chose lower vinylogues **N** and **O** of the partial structures of **1** and **2** as objectives of the present study. Parallel experiments have been carried out on photochemically generated nitrenes and persistent nitroxides as spin center X. Since a preliminary study showed that $p,p'$-dinitroxide **O'** readily undergoes polymerization as soon as solvent is removed,[4] isomeric $\beta,\beta$-dimethylvinylidene derivatives **O** with additional steric protection have been employed in this work.[5]

$p,p'$-, $m,p'$-, and $m,m'$-**C** might also be considered as vinylogues or phenylogues of trimethylenemethane (**4**), tetramethyleneethane (**5**), and pentamethylenepropane (**6**), respectively. Since the ground spin states of **5** and **6** are still subjects of some controversy in contrast to the well-established triplet of **4**,[6] we thought the delineation of the manner in which the electron spins would couple in isomeric series of **N** and **O** might shed light on the discussion of the ground-state spins of **5** and **6**.

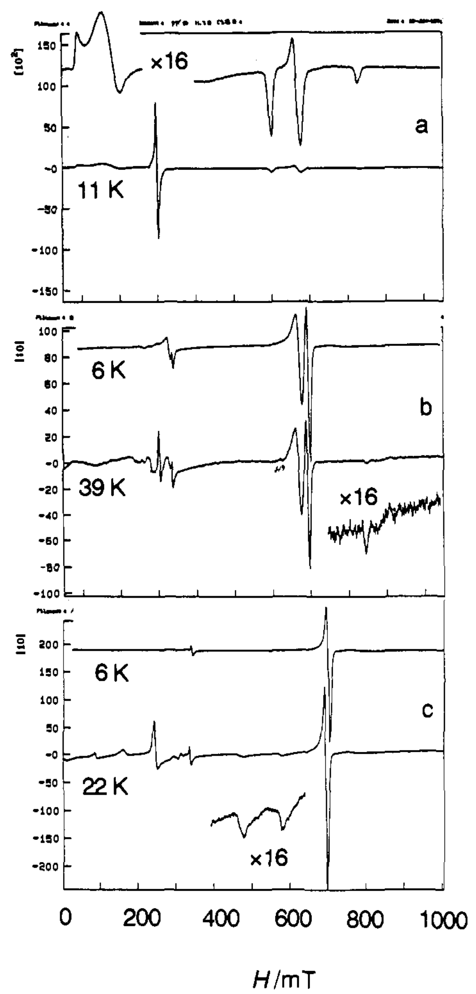


**Figure 1.** X-Band EPR spectra at several temperatures due to (a) $p,p'$-, (b) $m,p'$-, and (c) $m,m'$-**N** generated by photolysis of the corresponding **A** in an EPR cavity at cryogenic temperatures. The X,Y transitions due to triplet mononitrenes formed fortuitously are conspicuous at 660–690 mT.

## Results

**Synthesis of Vinylidenebis(azidobenzenes) (A).** Three isomeric bis(bromophenyl)methylcarbinols were treated with $p$-toluenesulfonic acid in benzene to give 1,1-bis(bromophenyl)ethylenes which in turn were lithiated and treated with $p$-toluenesulfonazide. The 1,1-bis(azidophenyl)ethylenes **A** thus formed were purified by chromatography on silica gel.

**Synthesis of Vinylidenebis(*N*-*tert*-butyl-*N*-oxyanilines) (O and O').** The dimethyldibromo compounds were obtained by dehydration of the corresponding isopropyl carbinols and lithiated with 4 equiv of *tert*-butyllithium and allowed to react with 2.5 equiv of 2-methyl-2-nitrosopropane to give the hydroxyamines which were then treated with excess $Ag_2O$ to give the corresponding dinitroxides **O**. Purification was made by chromatography on silica gel and reprecipitation from $n$-hexane to give analytically pure samples. Similarly 1,1-bis(bromophenyl)ethenes were lithiated and allowed to react with 2-methyl-2-nitrosopropane to give the hydroxyamines. On treatment with excess $Ag_2O$ in ether, the $m,m'$ isomer gave the expected dinitroxide $m,m'$-**O'**. The $p,p'$ isomer gave an ether solution which showed an expected five-line EPR hyperfine structure. When the solution was concentrated, however, the residue was an insoluble polymeric powder difficult to characterize further.

**EPR Spectra of Vinylidenebis(phenylnitrene) (N).** X-Band EPR spectra as reproduced in Figure 1 were obtained by photolysis of

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[3] (a) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722. (b) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. (c) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (d) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147. (e) Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, Y.; Itoh, K.; Miko, F.; Sawaki, Y.; Izuoka, A.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1990**, *112*, 4074. (f) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238. (g) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890. (h) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, *113*, 9235. Nakamura, N.; Inoue, K.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 1484.

[4] Ishida, T. Ph.D. Dissertation, University of Tokyo, 1991.

[5] A preliminary report on the isomeric **O** appeared in: Matsumoto, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 5448. $p,p'$- and $m,m'$-**N** in this paper correspond to **6** and **8** in: Ling, C.; Minato, M.; Lahti, P. M. *J. Am. Chem. Soc.*, following paper in this issue.

[6] (a) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. (b) Roth, W. R.; Erker, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503. (c) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (d) Borden, W. T., Ed.; *Diradicals*; Wiley: New York, 1982. (e) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072. (f) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A.; Merrill, R. A.; Duchamp, J. C.; Zilm, K. W. *J. Am. Chem. Soc.* **1991**, *113*, 2318.

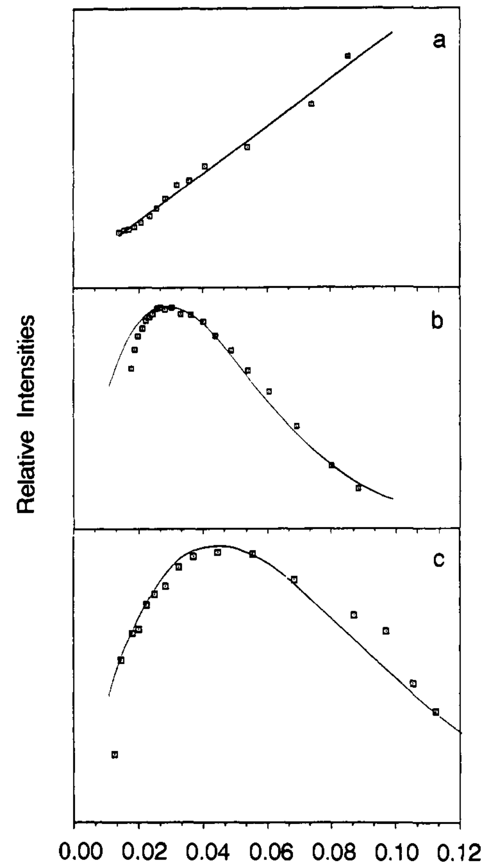

**Figure 2.** Temperature dependences of the signal intensities due to the quintet states of (a) *p,p′*-, (b) *m,p′*-, and (c) *m,m′*-N.

solutions of A in 2-methyltetrahydrofuran (MTHF) at 6 K with a high-pressure mercury arc through a Pyrex filter. The spectrum from *p,p′*-A (Figure 1a) is very similar to those of reported quintet dinitrenes;[7,8] peaks are at 830, 602, and 301 mT. A peak characteristic of the X,Y transition of a triplet mononitrene was also observed at 665 mT. By assuming that the highest- and next-highest-field resonances of weakly interacting dinitrenes in quintet states were assigned to the transitions parallel to the $z$ principal axis from $m_s = -2$ to $m_s = -1$ and $y$ principal axis from $m_s = 1$ to $m_s = 2$ sublevels, respectively, and applying a third-order perturbation theory,[8a] their resonance fields were estimated by eq 1,[8,9] where $\gamma = D$, $\delta = 3E^2/2$, and $\lambda = 4\gamma\delta$ for the $z$ transition,

$$H = H_0 + 3\gamma + \delta/(H_0 + 3\gamma) - \lambda/H_0^2 \qquad (1)$$

and $\gamma = (D + 3E)/2$, $\delta = 3(D - E)^2/8$, and $\lambda = -4\gamma\delta$ for the $y$ transition. The zero-field splitting (ZFS) parameters of *p,p′*-N were computed to be $D = 0.154$ and $E = -0.006$ cm$^{-1}$. Temperature dependence of the signals due to the quintet state is reproduced in Figure 2a. The observed plots obeyed a Curie law in the temperature range 11–90 K showing that the quintet is either a ground state or degenerate with a singlet state. Since any additional signal due possibly to an excited triplet state was not detected, the latter possibility was regarded to be remote.

In the case of *m,p′*-A (Figure 1b), only a pair of signals due to triplet mononitrenes as detected at 669 and 694 mT (corresponding to the nitrene groups para and meta to the vinylidene group, respectively). As the temperature was raised in the dark after the photolysis, signals at 306, 341, 618, and 847 mT characteristic of a quintet grew in, reached their maximum intensities at ca. 40 K, and then decreased in their intensities (Figure 2b), indicating that the observed quintet is thermally populated. The zero-field splitting (ZFS) parameters of the quintet were computed to be $D = 0.159$ and $E = 0.009$ cm$^{-1}$ on the basis of eq 1.

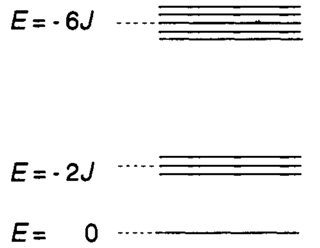

**Figure 3.** The state energy diagram showing the ground singlet and excited triplet and quintet states higher in energy by $-2J$ and $-6J$, respectively, from two weakly interacting triplets.[9]

**Table I.** Energy Gaps between the Singlet and High-Spin States in Isomeric Dinitrenes **N** and Dinitroxides **O**[a]

| | N | O | | | |
|---|---|---|---|---|---|
| | $E_{S-Q}{}^b$/ cm$^{-1}$ (cal/mol) | $E_{S-T}{}^c$/ cm$^{-1}$ (cal/mol) | $\theta$/K | GS from VB | GS from MO |
| *p,p′* | ≫0<br>(≫0) | 10.6<br>(30.3) | −2.0 | $S = 1$ | nondisjoint |
| *m,p′* | −42.0<br>(−120.1) | −3.4<br>(−9.7) | −2.0 | $S = 0$ | disjoint |
| *m,m′* | −26.2<br>(−74.9) | −1.8<br>(−5.1) | −2.1 | $S = 1$ | doubly disjoint |
| *m,m′*[d] | | −2.4<br>(−6.9) | −3.5 | $S = 1$ | doubly disjoint |

[a] +/− signs represent triplet/singlet ground states, respectively. [b] The energy gap between the two states $E_{S-Q} = 6J$. [c] The energy gap between the two states $E_{S-T} = 2J$. [d] **O′**.

Similarly, only a signal due to a triplet was detected at 694 mT after photolysis of *m,m′*-A at 7 K (Figure 1c). As the temperature was raised in the dark after photolysis, several signals characteristic of a quintet started to grew in at 247, 580 mT, etc. (Figure 1c). Since the highest-field signal was difficult to read, ZFS constants remained to be determined. The temperature dependence of the signal intensities due to the quintet revealed a maximum at ca. 20 K (Figure 2c).

According to a theory of two weakly interacting triplets,[9] antiferromagnetic interaction ($J < 0$) leads to a ground singlet state with excited triplet and quintet states higher in energy by $-2J$ and $-6J$, respectively, from the ground state, where $J$ is the exchange integral of two electrons, one on each nitrene centers (Figure 3).

The observed data were fitted with a Bleaney–Bowers-type equation (eq 2)[10] describing the temperature dependence of the

$$I_Q = \frac{C}{T} \frac{5 \exp(6J/RT)}{1 + 3 \exp(2J/RT) + 5 \exp(6J/RT)} \qquad (2)$$

signal intensity $I_Q$ due to the excited quintet state (Figure 2, b and c).[7] The energy gaps $\Delta E_{S-Q} = 6J$ thus obtained are summarized in Table I.

**EPR Spectra of 1,1-Bis(*N*-oxy-*tert*-butylaminophenyl)-2-methylpropenes (O).** X-Band EPR spectra of **O** in toluene at room temperature consisted of unperturbed five lines ($g = 2.006$, $|J| > |a_N| = 11.2$ G). In frozen toluene at 5–10 K, broad slightly structured spectra were obtained as shown in Figure 4, showing that the dipolar interaction between the nitroxides was unexpectedly small: spectral widths as a measure of $2D$ were less than 90 G, but $\Delta m_s = 2$ transitions for triplet species were clearly observed at $g = 4$. The signals were too small to study the temperature dependence of their intensities.

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(7) Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33. Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

(8) (a) Itoh, K. *Abstract of Papers* (in Japanese)., 6th ESR Symposium of the Chemical Society of Japan, Kyoto, Oct. 1967; p 117. (b) Wasserman, E.; Murray, R. W.; Yager, W. A. Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(9) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

(10) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

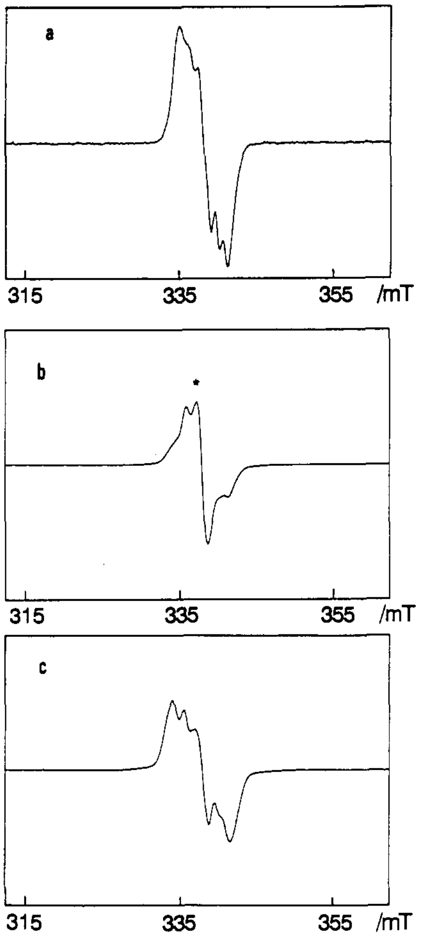

**Figure 4.** X-Band EPR spectra of (a) *p,p'*-, (b) *m,p'*-, and (c) *m,m'*-**O** in frozen MTHF at cryogenic temperatures.

It was difficult to simulate the observed spectra even by overlapping the fine structure with anisotropic *g* tensors and hyperfine couplings with the nitrogen nuclei. Probably several conformers with slightly different EPR parameters have to be taken into consideration.

**Magnetic Measurements on Vinylidenebis(*N*-*tert*-butyl-*N*-oxyanilines) (O and O').** The magnetic susceptibility ($\chi$) was measured for microcrystalline samples of **O** (on a SQUID susceptometer at 0.5 T) and **O'** (on a Faraday balance at 1.0 T) in the temperature range 5–300 K. The results are expressed in terms of $\mu_{\rm eff}/\mu_B$ versus temperature plots in Figure 5, where $\mu_{\rm eff}$ and $\mu_B$ are the effective magnetic moment and the Bohr magneton, respectively. The $\mu_{\rm eff}$ values approaching 2.45 $\mu_B$ at room temperature are strongly indicative of near degeneracy of singlet and triplet states in all the three isomers at ambient temperature, since $\mu_{\rm eff}$ values are given by:

$$\mu_{\rm eff}^2 = 3k\chi T/N = \sum_i n_i \mu_{{\rm eff}i}^2 \Big/ \sum_i n_i \qquad (3)$$

where

$$\mu_{{\rm eff}i}^2 = g^2(i - 1)(i + 1)\mu_B^2/4 \qquad (4)$$

and $n_i$ stands for the population of the state in multiplicity $i$. For degenerate singlet/triplet species, $\mu_{\rm eff}^2 = g^2\{1 \times 0 + 3 \times 1\ (1 + 1)\}\mu_B^2/4 = 6g^2\mu_B^2/4$. A purely triplet species should have given a $\mu_{\rm eff}/\mu_B$ value of 2.83 ($i$ = 3 in eq 4). A sharp decrease in the $\mu_{\rm eff}$ values at the lowest temperature represents the antiferromagnetic exchange coupling between diradical molecules. The presence of a maximum at 16 K in the plot for the *p,p'*-**O** corresponds to an increased population of a triplet relative to a singlet at lower temperatures (Figure 5a), showing that a triplet should be a ground state of the *p,p'* isomer of **O**. Gradual decreases of the plots during intermediate temperature range in the *m,p'*- and *m,m'*-**O** are suggested to be due to antiferromagnetic interaction between the radical centers within the molecules (Figure 5, b and c). For a singlet–triplet system, the behavior of $\chi$ with respect to temperature can be described according to a modified Bleaney–Bowers equation[10] (eq 5), where $N$ is number of the spins

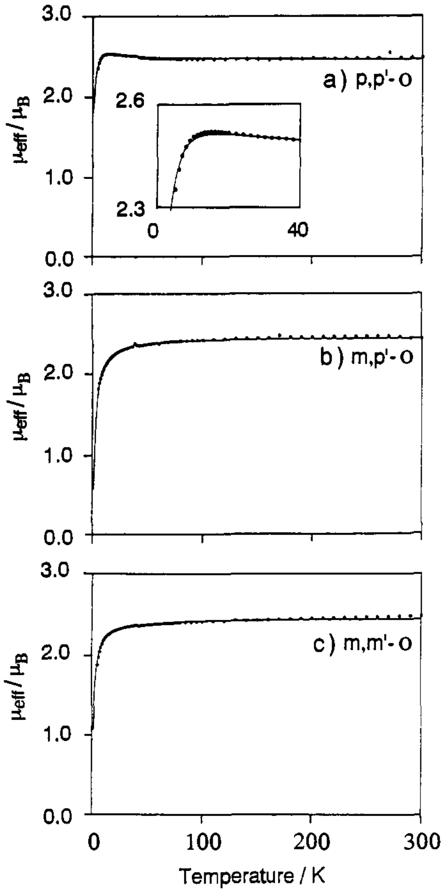

**Figure 5.** Plots of the observed $\mu_{\rm eff}/\mu_B$ versus temperature for (a) *p,p'*-, (b) *m,p'*-, and (c) *m,m'*-**O**. The best fit curves were obtained when empirical factor *F*'s in eq 5 were 0.97, 0.88, and 0.94 for the *p,p'*-, *m,p'*- and *m,m'*-**O**, respectively.

$$\chi = F\frac{2Ng^2\mu_B^2}{k(T - \theta)[3 + \exp(-2J/kT)]} \qquad (5)$$

per unit weight, $g$ is the isotropic $g$ factor, and a weak interradical interaction is taken into account by means of a Weiss temperature $\theta$. The plots of $\mu_{\rm eff}/\mu_B$ versus temperature were analyzed with a theoretical curve, and the parameters obtained were refined by a least-squares methods on the program SALS[11] to give results summarized in Table I. Whereas the dinitroxides **O** and **O'** were analytically pure (see Experimental Section), the fittings of the theoretical curve to the real experimental data were improved when an empirical factor $F$ was introduced in eq 5 for correcting slight reduction in the effective magnetic moment of the samples used for the magnetic measurements by the presence of nondiradical impurities;[11] *F*'s were 0.97, 0.88, and 0.94 for the *p,p'*-, *m,p'*- and *m,m'*-**O**, respectively. It was 0.89 for *m,m'*-**O'**.

## Discussion

It has been established in this study that the open-shell centers, one on each phenyl ring in 1,1-diphenylethylenes **N** and **O**, couple ferro- and antiferromagnetically when they are *p,p'* on the one hand and *m,p'* and *m,m'* on the other, respectively. In *p,p'*-**N**, strong EPR signals due to the quintet dinitrene that followed a

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(11) Nakagawa, T.; Oyanagi, Y. SALS Program System for Nonlinear Least-Square Fitting in Experimental Science; In *Recent Developments in Statistical Inference and Data Analysis*; Matsushita, K., Ed.; North Holland: Amsterdam, 1980; pp 221–225. We thank a referee for pointing out a caution to be paid to the multiparameter fittings to magnetic susceptibilities for impure samples.

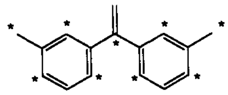


**Figure 6.** Figurative presentation of the VB theory[6] predicting $S = (9 - 7)/2 = 1$ in *m,m'*-C.

Curie law were observed. Since signals due to lower spin states were not detected over the temperature range 11–90 K, the ground state must be a quintet; it was not possible to determine from a Boltzmann distribution of the spins how strongly the two triplet nitrene units interact ferromagnetically through the vinylidenebis(*p*-phenyl) coupler.

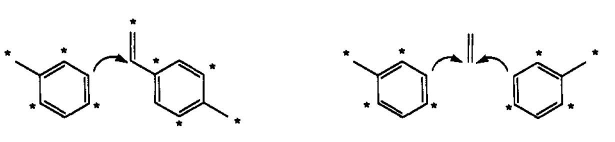
Both dipole–dipole and exchange couplings between the nitroxide functions are very weak in all the three isomers. By taking advantage of this attenuated interaction in **O** and the wider temperature range (5–300 K) applicable to the persistent dinitroxides, it was possible to obtain the absolute $J$ value even in the *p,p'* topology. Since the small energy gap values $2J$ are still estimated to be larger than the zero-field splittings of the triplet states, the application of eq 2 to the present system is justified.

Whereas the absolute values of the exchange coupling $J$ in isomeric **N** are four to five times as large as those of **O**, the signs are in parallel. There are at least two reasons conceivable for the systematic reduction in the interaction in **O** compared with **N**. Firstly, interaction between two spins in non-Kekulé systems takes place via polarization of the $\pi$-bonds intervening the two radical centers;[1] high-spin states would result when they are placed in phase with the spin polarization of the intervening $\pi$-bonds. It has been shown that, in phenyl nitroxides, the electron spins are much more localized in the nitroxide moieties than in hydrocarbon radicals.[12] Therefore, the degree of spin polarization on the phenyl rings must be reduced somewhat in **O**. Secondly, MM2 calculations on 1,1-diphenylethylene and 1,1-diphenyl-2-methylpropene give an estimate of the propeller-type torsional angle $\varphi$ of the phenyl rings out of the vinylidene and dimethylvinylidene planes to be 40° and 54°, respectively. When the data of the *m,m'* isomers of **O** and **O'** are compared, the latter has the larger absolute $J$ value although the difference is not greater than twice as much. These two factors appear to attenuate the topological effect of the radical centers on the mode of the exchange coupling.

Using valence bond theory and a Pariser–Parr–Pople Hamiltonian, Ovchinnikov has derived a method of predicting the ground states of alternant hydrocarbons by counting starred and unstarred atoms.[13e] His conclusion is expressed in terms of eq 6:

$$S = (n^* - n)/2 \qquad (6)$$

where $S$ is the spin quantum number of the ground state, and $n^*$ and $n$ are respectively the number of starred and unstarred carbons. According to this rule, both *p,p'*- and *m,m'*-C have $n^* = 9$ and $n = 7$, and, therefore, triplet ground states $S = 1$ are predicted (Figure 6). *m,p'*-C has $n^* = n = 8$ and therefore a singlet ground state $S = 0$ is predicted. The validity of the extension of this rule to alternant nonhydrocarbons, in general, and nitrenes and nitroxides, in particular, has been amply demonstrated.[3f,14] Note that each nitroxide group should be counted once as a pseudoatom.[3f] For the **N** series, the localized $\sigma$-spin on the nitrogen atom which is strongly coupled to the $\pi$-spin via one-center exchange coupling has to be taken into account, and therefore the singlet and triplet states should correspond to the singlet and quintet states, respectively. The experimental results obtained in this study are consistent with this VB theory for the *p,p'* and *m,p'* isomers but contradictory to the predicted high-spin ground states of the *m,m'* isomers.



*m, p'*-C *m, m'*-C

**Figure 7.** The MO theory showing the singly disjoint *m,p'*-C and doubly disjoint *m,m'*-C.

**Table II.** Computed Energy Gaps between the Singlet and High-Spin States in Isomeric Dinitrenes N[15] and Dinitroxides O''

| | N<br>$E_{S-Q}$/cm$^{-1}$ | O''<br>$E_{S-T}$/cm$^{-1}$ | GS from VB | GS from MO |
|---|---|---|---|---|
| *p,p'* | 3000 | 750 | $S = 1$ | nondisjoint |
| *m,p'* | 840 | −610 | $S = 0$ | disjoint |
| *m,m'* | 1600 | 570 | $S = 1$ | doubly disjoint |

The Radhakrishnan rule states on the basis of spin polarization and superexchange interactions that, if an intervening orbital has zero or even electrons, the $\pi$-conjugated diradicals will be low spin. If it has odd electrons, the interaction will be ferromagnetic.[13g] Here again the *p,p'* and *m,p'* isomers are satisfactorily predicted to be high and low spin, respectively. The *m,m'* isomers have seven $\pi$-electrons between the open-shell centers and are predicted to be high spin, a prediction in conflict with the present results.

Borden and Davidson noted the localizability of the Hückel nonbonding MOs in governing the ground states of non-Kekulé hydrocarbons and proposed a theory predicting that, if the Hückel nonbonding MO's cannot be localized to different sets of atoms, the systems called nondisjoint are expected to have triplet ground states with the largest magnitude of the energy gap $\Delta E_{S-T}$.[6c,d] If localization is possible, the lowest singlet and triplet states of these disjoint systems should be nearly degenerate, and a singlet should become a ground state due to higher-order effects with small magnitude of $\Delta E_{S-T}$. In reference to this theory, *p,p'* and *m,p'* isomers of **N** and **O** are, respectively, nondisjoint and disjoint as shown in Figure 7. The experimental results are in good agreement with this MO theory. Furthermore, since *m,m'* diradicals are "doubly disjoint" in a sense that the carbons with substantial positive spin density are separated by three carbons (Figure 7), they are predicted to have singlet ground states with the smallest magnitude of the energy gap of all. The experimental results that the *m,m'* isomers of **N**, **O**, and **O'** all have singlet ground states are in line with this perturbational MO theory.

There are some semiempirical calculations available for the $\Delta E_{S-Q}$ and $\Delta E_{S-T}$ values of **N** and **O**, respectively (Table II). AM1-CT calculations have predicted the ground states of all the isomeric **N** to be quintet by a good margin.[15] AM1-UHF calculations on sterically unprotected dinitroxides **O''** give the values in the order of a kcal/mol, and the sign is not in agreement with the observed one for *m,m'* isomer (Table II). However, if the numerical values in Table II are referenced to a certain positive value and contracted, they show a trend in line with the experimental data in a sense that the magnitudes of $\Delta E_{S-Q}$ and $\Delta E_{S-T}$ are positive by a large margin in *p,p'*, considerably negative in *m,p'*, and negative by a smallest margin in *m,m'* isomers. Higher order computations are necessary for more quantitative discussion.

The question may be raised if the topological/through-bond consideration would be enough to discuss the exchange coupling in **N** and **O**. In the 1,1-diphenylethylene chromophore, through-space interactions may have to be taken into account. These effects, if any present, would be most significant at the sites between the two ortho carbons and two ipso carbons, one on each phenyl ring in the planar ($\varphi = 0°$) and perpendicular ($\varphi = 90°$) conformations, respectively. When inspected in reference to McConnell's theory of Heitler–London spin exchange between

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(12) Aurich, H. G.; Deuschle, E.; Lotz, I. *J. Chem. Res., Synop.* **1977**, 248.

(13) (a) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265. (b) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (c) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. (d) Itoh, K. *Bussei* (in Japanese) **1971**, *12*, 635. (e) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *10*, 297. (f) Dougherty, D. A. *Acc. Chem. Res.* **1990**, *24*, 88. (g) Radhakrishnan, T. P. *Chem. Phys. Lett.* **1991**, *181*, 455.

(14) Tyutyulkov, N.; Polansky, O. E. *Chem. Phys. Lett.* **1987**, *139*, 281. Tyutyulkov, N.; Ivanov, Ts.; Shopov, I. S.; Polansky, O. E.; Olbrich, G. *Int. J. Quantum Chem.* **1988**, *34*, 361. Tyutyulkov, N.; Karabunarliev, S.; Ivanov, Kh. *Mol Cryst. Liq. Cryst.* **1989**, *176*, 139. Tukada, H.; Mutai, K.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1159.

(15) Lahti, P. M.; Ichimura, A. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 125. Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030.

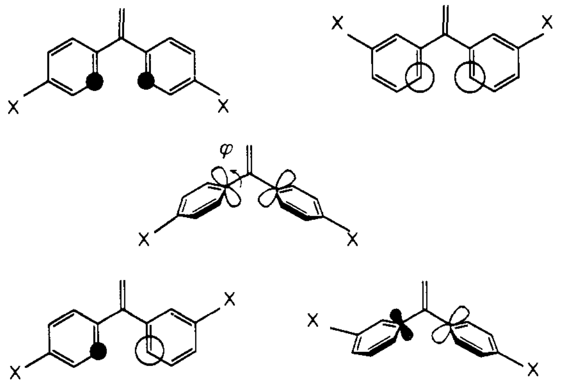


**Figure 8.** Potential intramolecular through-space interactions in 1,1-vinylidenebis(phenyl radicals) in various conformations. Open and shaded circles correspond to the π-orbitals with positive and negative spin densities, respectively.

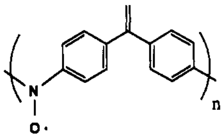
site a of positive spin density and site b of negative spin density,[16] the interaction at these sites contains always the spins of the same sign for the symmetrical *p,p'* and *m,m'* isomers (see Figure 8), while the interaction of the spins of opposite sign is involved in the unsymmetrical *m,p'* isomer. Therefore, the through-space interactions are expected to be antiferromagnetic in *p,p'*- and *m,m'*-**N** and -**O** and ferromagnetic in *m,p'*-**N** and -**O**. Interestingly, these trends are opposite to those of the topological/through-bond effects mainly discussed in this paper and might serve as a third factor attenuating the latter effects. In reality, however, the ground-state conformations of **N** and **O** are estimated to be propeller-shaped (φ = 40–54°; vide supra). Under these conditions, the two orbitals under consideration become just about perpendicular or orthogonal to each other. Therefore, the discussion in reference to McConnell's theory may not lead to a straightforward conclusion.

There are two more messages from this work. It is pointed out in the introduction that *p,p'*-, *m,p'*-, and *m,m'*-**C** might be related in connectivity to trimethylenemethane (**4**), tetramethyleneethane (**5**), and pentamethylenepropane (**6**), respectively. The ground-state spins of **5** and **6** are still subjects of controversy in contrast to the well-established triplet of **4**.[6] The results that the *p,p'* systems always have high-spin ground states are consistent with the triplet **4**. Antiferromagnetic interaction found in the *m,p'* and *m,m'* topology suggests that the ground states of **5** and **6** may be singlet. Since the electron spins are more localized in the nitroxide moieties and the π-systems are enlarged in **N** and **O**, the conclusion should be viewed with some caution. However, measurements of absolute $\mu_{\text{eff}}$ values and their temperature dependence over a wide temperature range would be a useful method for distinguishing between a triplet ground state and a nearly degenerate singlet/triplet state, in general, and solving the controversy in **5** and **6**, in particular.

Secondly, concerning the molecular design and super-high-spin polymers, the coupling in **1** and **2** is estimated to be ferromagnetic only when radical centers X, e.g., N(*t*-Bu)O•, are all at the para position. Even in these cases, however, the interaction among the neighboring X's should not be very strong relative to *kT* at ambient temperature. "All-meta"-substituted polymers are related in connectivity to *m,m'* isomers of **N** and **O** and therefore predicted to be low spin. This conclusion contradicts the Ovchinnikov and Radhakrishnan rules. Polymers like **7** can be high spin but do not appear to have any merit over **3**.

## Experimental Section

**(A) ESR Spectroscopy and Magnetic Measurements.** ESR spectra were recorded on a Bruker ESP 300 X-band (9.48 GHz) spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter.



**7**

An Air Products LTD-3-110 liquid helium transfer system was fitted for the low-temperature measurements.

Magnetic susceptibility data for microcrystalline samples of **O** and **O'** were obtained on a Quantum Design MPMS2 SQUID susceptometer at the field strength of 0.5 T and an Oxford Faraday balance at 1.0 T, respectively, in the temperature range 5–300 K.

**(B) Other Instrumentation.** $^1$H (270 MHz) and $^{13}$C (68.0 MHz) NMR spectra were obtained on a JEOL GX-270 spectrometer. IR and mass spectra were obtained on Hitachi 270-30 and JEOL JMS D-300 spectrometers, respectively.

**(C) Photolysis of Solid Solutions of A in MTHF in an ESR Cavity.** A 2-mM solution of **A** in MTHF was sealed in an EPR sample tube by at least three freeze–pump–thaw cycles. Irradiation in an EPR cavity was made at the cryogenic temperature for ca. 1 h with an Ushio high-pressure mercury source (500 W) through water (10 cm) and Pyrex glass filters. EPR measurements were performed in the dark after the photolysis.

(D) **AM1-UHF and MM2 Computations.** Molecular orbital calculations by the AM1 method were carried out on a HITAC M-680-H computer system at the Computer Center of the University of Tokyo (CCUT) with MOPAC Version 5.01;[17] AM1 optimizations were carried out using unrestricted Hartree–Fock (UHF) wave functions. Molecular mechanics calculation were carried out on a DEC system 5830 with the MM2 (85) program.[18]

(E) **Materials.** The solvents diethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, benzene, and toluene used for the reactions, and spectral measurements were all distilled under high-purity $N_2$ after drying with sodium/benzophenone ketyl. All reactions were stirred under an atmosphere of argon. Anhydrous magnesium sulfate was used as the drying agent. Neutral workup refers to quenching the reaction with aqueous ammonium chloride, washing the organic layer with water, drying, filtering, and concentrating in vacuo. Basic workup included aqueous sodium bicarbonate instead of ammonium chloride. Column chromatography was performed on silica gel (Wako Gel C 200) or alumina (Wako Activated Alumina, 200 mesh).

**1,1-Bis(4-bromophenyl)ethanol.** To a solution of 9.45 g (40.1 mmol) of *p*-dibromobenzene in 100 mL of THF at −78 °C was added in 30 min 25 mL (40 mmol) of 1.6 M *n*-butyllithium in hexane. Ethyl acetate (1.90 g, 21.6 mmol) was added at this temperature. The mixture was warmed overnight to ambient temperature. Neutral workup gave a yellow oil which was chromatographed on an alumina column eluted with hexane/dichloromethane (4:1 v/v) giving 4.99 g (70.0%) of 1,1-bis(4-bromophenyl)ethanol as yellow oil. $^1$H NMR (CDCl$_3$) δ 1.90 (s, 3 H), 2.14 (s, 1 H), 7.26 (d, *J* = 8 Hz, 4 H), 7.44 (d, *J* = 8 Hz, 4 H).

**1,1-Bis(4-bromophenyl)ethene.** A solution of 4.74 g (13.3 mmol) of 1,1-bis(4-bromophenyl)ethanol and 0.34 g of *p*-toluenesulfonic acid in 50 mL of benzene was refluxed for 2 h. Basic workup gave a yellow solid. Chromatography on silica gel with hexane elution gave 4.13 g (91.7%) of 1,1-bis(4-bromophenyl)ethene as white crystals, mp 75–81 °C. $^1$H NMR (CDCl$_3$) δ 5.46 (s, 2 H), 7.18 (d, *J* = 8.4 Hz, 4 H), 7.46 (d, *J* = 8.4 Hz, 4 H).

**1,1-Bis(4-azidophenyl)ethene (*p,p'*-A).** To a solution of 0.88 g (2.60 mmol) of the ethene in 20 mL of THF at −78 °C was added 6.1 mL (10.37 mmol) of 1.7 M solution of *tert*-butyllithium in pentane. After 25 min, a solution of 1.05 g (5.32 mmol) of *p*-toluenesulfonyl azide in 5 mL of THF was added. After 3 h, neutral workup gave a reddish solid. Chromatography on silica gel eluted with hexane gave 0.50 g (73.5%) of *p,p'*-**A** as yellow crystals, mp 88–94 °C. $^1$H NMR (CDCl$_3$) δ 5.81 (s, 2 H), 6.97 (d, *J* = 8 Hz, 4 H), 7.30 (d, *J* = 8 Hz, 4 H). Anal. Calcd for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.04. Found: C, 64.23; H, 4.14; N, 31.16. IR (KBr disks) 2139 ($N_3$), 1599, 1506, 1298, 839, 810 cm$^{-1}$.

**1-(3-Bromophenyl)-1-(4-bromophenyl)ethanol.** To a solution of 9.43 g (40.0 mmol) of *p*-dibromobenzene in 80 mL of THF at −78 °C was added 25 mL (40 mmol) of 1.6 M *n*-butyllithium in hexane and, after 1 h, a solution of 7.95 g (40 mmol) of 3-bromoacetophenone in 10 mL of THF. After 2 h, neutral workup followed by chromatography on alumina eluted with hexane/dichloromethane (1:1, v/v) gave 7.24 g (50.8%) of 1-(3-bromophenyl)-1-(4-bromophenyl)ethanol as yellow oil.

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(16) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. Izuoka, A.; Murata, S.; Sugawara, T.; Iwamrua, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786. Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293. Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(17) MOPAC Version 5, J. J. P. Stewart, QCPE No. 455; Revised as Version 5.01 by Prof. T. Hirano of Ochanomizu Women's University.

(18) The program was obtained from QCPE.

$^1$H NMR (CDCl$_3$) $\delta$ 1.91 (s, 3 H), 2.15 (s, 1 H), 7.18 (t, $J$ = 7.8 Hz, 1 H), 7.27 (d, $J$ = 8.6 Hz, 3 H), 7.38 (d, $J$ = 7.8 Hz, 1 H), 7.45 (d, $J$ = 8.6 Hz, 2 H), 7.58 (s, 1 H).

**1-(3-Bromophenyl)-1-(4-bromophenyl)ethene.** Dehydration was carried out in a manner similar to that for the *p,p'* isomer to give a yellow oil in 34.0% yield. $^1$H NMR (CDCl$_3$) $\delta$ 5.45 (s, 1 H), 5.47 (s, 1 H), 7.16–7.22 (m, 4 H), 7.33 (m, 1 H), 7.46–7.50 (m, 4 H).

**1-(3-Azidophenyl)-1-(4-azidophenyl)ethene (*m,p'*-A)** was obtained from the dibromoethene in a manner similar to that used for the corresponding *p,p'*-dibromo derivative in 59.2% yield as pale yellow oil. $^1$H NMR (CDCl$_3$) $\delta$ 5.44 (s, 1 H), 5.48 (s, 1 H), 6.98–7.01 (m, 4 H), 7.08 (d, $J$ = 7.8 Hz, 1 H), 7.29–7.35 (m, 3 H). $^{13}$C NMR (CDCl$_3$) $\delta$ 115.0, 118.4, 118.8, 118.9, 124.9, 129.5, 129.6, 137.6, 139.7, 140.1, 143.1, 148.3. IR (neat) 2110 (N$_3$), 1601, 1578, 1505, 1487, 1292, 899, 839, 789, 716 cm$^{-1}$.

**1,1-Bis(3-bromophenyl)ethanol.** To a solution of 3.40 g (14.4 mmol) of *m*-dibromobenzene in 30 mL of THF at −78 °C was added 9.0 mL (14.4 mmol) of 1.6 M *n*-butyllithium in hexane. After 25 min, a solution of 2.88 g (14.5 mmol) of 3-bromoacetophenone in 5 mL of THF was added. After 2 h at ambient temperature, neutral workup and chromatography on alumina eluted with hexane/dichloromethane (1:1, v/v) gave 2.02 g (5.67 mmol) of 1,1-bis(3-bromophenyl)ethanol as yellow oil. $^1$NMR (CDCl$_3$) $\delta$ 1.91 (s, 3 H), 2.20 (s, 1 H), 7.18 (t, $J$ = 8 Hz, 2 H), 7.29 (d, $J$ = 8 Hz, 2 H), 7.39 (d, $J$ = 8 Hz, 2 H), 7.60 (s, 2 H).

**1,1-Bis(3-bromophenyl)ethene** was obtained from the ethanol by dehydration in a manner similar to that used for the corresponding 4-bromophenyl derivative in 68.8% as colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 5.49 (s, 2 H), 7.20–7.23 (m, 4 H), 7.44–7.47 (m, 4 H).

**1,1-Bis(3-azidophenyl)ethene (*m,m'*-A)** was obtained from the dibromoethene in a manner similar to that used for the corresponding 4-bromophenyl derivative in 61.5% yield as colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 5.50 (s, 2 H), 6.97 (t, $J$ = 2.0 Hz, 2 H), 7.01 (ddd, $J$ = 7.7 Hz, 2.0 Hz, 1.2 Hz, 2 H), 7.07 (dt, $J$ = 7.7 Hz, 1.2 Hz, 2 H), 7.33 (t, $J$ = 7.7 Hz, 2 H). IR (neat) 2120 (N$_3$), 1601, 1577, 1483, 1442, 1288, 885, 786 cm$^{-1}$.

**1,1-Bis(4-bromophenyl)-2-methylpropanol.** To a solution of 11.80 g (50.0 mmol) of *p*-dibromobenzene in 100 mL of THF at −78 °C was added a 1.6 M hexane solution of *n*-butyllithium (31.25 mL, 50 mmol). After 10 min, 2.9 g (25.3 mmol) of methyl isobutyrate was added. After 2 h, neutral workup followed by chromatography on alumina eluted with hexane/dichloromethane (9:1, v/v) gave 6.88 g (71.6%) of 1,1-bis(4-bromophenyl)-2-methylpropanol as white crystals, mp 139–142 °C. $^1$H NMR (CDCl$_3$) $\delta$ 0.87 (d, $J$ = 7.0 Hz, 6 H), 2.79 (septet, $J$ = 7.0 Hz, 1 H), 7.33 (d, $J$ = 8.8 Hz, 4 H), 7.41 (d, $J$ = 8.8 Hz, 4 H). Anal. Calcd for $C_{16}H_{16}OBr_2$: C, 50.04; H, 4.20; Br, 41.61. Found: C, 50.28; H, 4.38; Br, 42.42.

**1,1-Bis(4-bromophenyl)-2-methylpropene.** A solution of 6.88 g (17.9 mmol) of the propanol and 1.0 g of *p*-toluenesulfonic acid in 100 mL of benzene was refluxed for 1 h. Basic workup followed by chromatography on silica gel eluted with hexane gave 6.15 g (93.9%) of 1,1-bis(4-bromophenyl)-2-methylpropene as a white solid, mp 99–102 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.79 (s, 6 H), 6.97 (d, $J$ = 8.4 Hz, 4 H), 7.40 (d, $J$ = 8.4 Hz, 4 H). Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85; Br 43.65. Found: C, 52.32; H, 3.84; Br, 44.67. IR (KBr disks) 2909, 1483, 1101, 1070, 822 cm$^{-1}$.

**1,1-Bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]-2-methylpropene.** To a solution of 1.29 g (3.52 mmol) of the dibromopropene in 30 mL of THF at −78 °C was added 8.8 mL (15.0 mmol) of 1.7 M *tert*-butyllithium in pentane. After 1 h, a solution of 0.70 g (8.0 mmol) of 2-methyl-2-nitrosopropane in 20 mL of THF was added slowly. After 10 h of stirring at ambient temperature and neutral workup, a white solid was recrystallized from hexane/ether to give 0.23 g (17%) of 1,1-bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]-2-methylpropene as a white solid, mp 183 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.12 (s, 18 H), 1.79 (s, 6 H), 6.01 (s, 2 H), 7.00 (d, $J$ = 8.6 Hz, 4 H), 7.14 (d, $J$ = 8.6 Hz, 4 H). Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.30. Found: C, 74.26; H, 8.65; N, 7.30. IR (KBr disks) 3239 (OH), 2978, 1603, 1499, 1362, 1200, 959, 839 cm$^{-1}$.

**1-(4-Bromophenyl)-2-methyl-1-propanone.** To a solution of 11.84 g (50.2 mmol) of *p*-dibromobenzene in 100 mL of THF at −78 °C was added 31.25 mL (50.0 mmol) of 1.6 M *n*-butyllithium in hexane. After 20 min, 4.5 mL (50.1 mmol) of isobutyronitrile was slowly added. After 1 h at ambient temperature, dilute hydrochloric acid and ether were added. Basic workup followed by chromatography on silica gel gave 7.76 g (68.0%) of 1-(4-bromophenyl)-2-methyl-1-propanone as yellow oil. $^1$H NMR (CDCl$_3$) $\delta$ 1.21 (d, $J$ = 6.6 Hz, 6 H), 3.49 (septet, $J$ = 6.6 Hz, 1 H), 7.61 (d, $J$ = 8.6 Hz, 2 H), 7.82 (d, $J$ = 8.6 Hz, 2 H).

**1-(3-Bromophenyl)-1-(4-bromophenyl)-2-methyl-1-propanol.** To a solution of 5.90 g (25.0 mmol) of *m*-dibromobenzene in 50 mL of THF at −78 °C was added 15.6 mL (25 mmol) of 1.6 M *n*-butyllithium in hexane. After 30 min, 5.68 g (25.0 mmol) of the (4-bromophenyl)propanone was added slowly. After overnight at ambient temperature, neutral workup followed by chromatography on alumina eluted with hexane gave 7.11 g (74.0%) of 1-(3-bromophenyl)-1-(4-bromophenyl)-2-methyl-1-propanol as a colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 0.87 (d, $J$ = 6.6 Hz, 6 H), 2.80 (septet, $J$ = 6.6 Hz, 1 H), 7.18 (t, $J$ = 7.9 Hz, 1 H), 7.29–7.44 (m, 6 H), 7.65 (s, 1 H).

**1-(3-Bromophenyl)-1-(4-bromophenyl)-2-methyl-1-propene** was obtained from the propanol as the *p,p'* isomer, a colorless oil in 77.7% yield. $^1$H NMR (CDCl$_3$) $\delta$ 1.78 (s, 6 H), 6.98 (d, $J$ = 8.4 Hz, 2 H), 7.03 (d, $J$ = 7.7 Hz, 1 H), 7.15 (t, $J$ = 7.7 Hz, 1 H), 7.26 (s, 1 H), 7.33 (d, $J$ = 7.7 Hz, 1 H), 7.41 (d, $J$ = 8.4 Hz, 2 H). IR (neat) 2909, 1590, 1557, 1485, 1198, 1073, 737, 718, 700, 677 cm$^{-1}$.

**1-[3-(*N*-Hydroxy-*tert*-butylamino)phenyl]-1-[4-(*N*-hydroxy-*tert*-butylamino)phenyl]-2-methyl-1-propene** was prepared as in the case of the 4,4' isomer. Purification was made by chromatography on silica gel eluted with dichloromethane to give a white solid in 5.1% yield, mp 182.8 °C (from hexane/ether). $^1$H NMR (CDCl$_3$) $\delta$ 1.15 (s, 18 H), 1.75 (s, 3 H), 1.76 (s, 3 H), 6.57 (d, $J$ = 7.7 Hz, 1 H), 6.79 (d, $J$ = 7.7 Hz, 1 H), 6.83 (d, $J$ = 8.4 Hz, 2 H), 6.91 (d, $J$ = 7.7 Hz, 1 H), 7.00 (d, $J$ = 8.4 Hz, 2 H), 7.11 (s, 1 H), 7.49 (bs, 2 H). Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.30. Found: C, 74.23; H, 8.30; N, 7.53. IR (KBr disks) 3227 (OH), 2984, 1599, 1576, 1480, 1389, 1200, 951, 893, 802, 714 cm$^{-1}$.

**1,1-Bis(3-bromophenyl)-2-methylpropanol** was obtained similarly to the *p,p'*-dibromo compound in 79.6% yield as a colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 0.87 (d, $J$ = 6.6 Hz, 6 H), 2.81 (septet, $J$ = 6.6 Hz, 1 H), 7.16 (t, $J$ = 7.9 Hz, 2 H), 7.32 (d, $J$ = 7.9 Hz, 2 H), 7.37 (d, $J$ = 7.9 Hz, 2 H), 7.67 (s, 2 H).

**1,1-Bis(3-bromophenyl)-2-methylpropene** was prepared similarly to *p,p'*-dibromopropene in 77.4% yield as a colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 1.78 (s, 6 H), 7.04 (d, $J$ = 8.0 Hz, 2 H), 7.16 (d, $J$ = 8.0 Hz, 2 H), 7.27 (s, 2 H), 7.34 (d, $J$ = 8.0 Hz, 2 H). IR (neat) 2909, 1590, 1557, 1470, 1198, 1073, 997, 785, 744, 700 cm$^{-1}$.

**1,1-Bis[3-(*N*-hydroxy-*tert*-butylamino)phenyl]-2-methylpropene** was prepared as in the case of the 4-isomer. Purification was made by chromatography on silica gel eluted with dichloromethane to give a white solid in 41.6% yield, mp 181–182 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.07 (s, 18 H0, 1.77 (s, 6 H), 6.56 (bs, 2 H), 6.82 (d, $J$ = 7.5 Hz, 2 H0, 7.03 (s, 2 H), 7.09 (d, $J$ = 7.5 Hz, 2 H), 7.14 (d, $J$ = 7.5 Hz, 2 H). Anal. Calcd for $C_{24}H_{34}N_2O_2$: C, 75.35; H, 8.96; N, 7.30. Found: C, 75.08; H, 8.99; N, 7.32. IR (KBr disks) 3227 (OH), 2984, 1599, 1576, 1480, 1389, 1200, 951, 893, 802, 714 cm$^{-1}$.

**1,1-Bis[(*N*-oxy-*tert*-butylamino)phenyl]-2-methyl-1-propenes (O).** To a solution of 100 mg (0.26 mmol) of the hydroxyamine in 10 mL of THF was added 0.4 g of freshly prepared silver oxide. After stirring for 1 h at ambient temperature, the residue was filtered off and the solution was concentrated under reduced pressure to obtain a red oil. Purification was carried out by chromatography on silica gel eluted with dichloromethane and precipitated with hexane. EPR (CH$_2$Cl$_2$) $g$ = 2.006, $a_N/2$ = 6.2 G (quintet).

***p,p'* Isomer:** mp 86–90 °C. Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.19; H, 8.46; N, 7.21. IR (KBr disks) 2980, 1669, 1603, 1489, 1356, 1190, 831 cm$^{-1}$.

***m,m'* Isomer:** mp 90–101 °C. Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.56; H, 8.60; N, 7.24. IR (KBr disks) 2982, 1640, 1590, 1561, 1478, 1370, 1217, 905, 802, 791, 714, 704 cm$^{-1}$.

***m,p'* Isomer:** mp 79–81 °C. Anal. Calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.73; H, 8.49; N, 7.12. IR (KBr disks) 2978, 1669, 1599, 1480, 1360, 1202, 1001, 905, 841, 801, 712 cm$^{-1}$.

**1,1-Bis[3-(*N*-hydroxy-*tert*-butylamino)phenyl]ethylene** was prepared from 1,1-bis(3-bromophenyl)ethylene[19] as in the case of ***m,m'*-O**. Purification was made by chromatography on silica gel eluted with dichloromethane, and recrystallization from hexane gave 0.96 g (27.8%) of 1,1-bis[3-(*N*-hydroxy-*tert*-butylamino)phenyl]ethylene as colorless crystals, mp 175–178 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.23 (s, 18 H), 5.41 (s, 2 H), 6.28 (br s, 2 H), 7.03 (m, 2 H), 7.2 (m, 6 H). $^{13}$C NMR (THF-$d_8$, 126 MHz) $\delta$ 26.5, 60.7, 113.5, 124.7, 124.9, 125.2, 127.6, 141.5, 151.7, 151.8. IR (KBr disks) 708, 736, 804, 1208, 1362, 1482, 1576, 1600, 2980, 3210 cm$^{-1}$. MS $m/z$ 354 (M$^+$, 8), 280 (20), 57 (100).

**1,1-Bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]ethylene** was prepared in 57% yield by starting from 1,1-bis(4-bromophenyl)ethylene in a method as described above for the *m,m'* isomer; mp 164–166 °C. $^1$H NMR (CDCl$_3$) $\delta$ 1.13 (s, 18 H), 5.36 (s, 2 H), 7.09 (d, $J$ = 8.8 Hz, 2 H), 8.02 (br, 2 H). $^{13}$C NMR (CDCl$_3$) $\delta$ 8 25.8, 60.5, 113.0, 124.3, 127.1, 137.8, 148.5, 148.8. IR (KBr disk) 850, 1202, 1364, 1506, 1608, 2980, 3240

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[19] Yamada, H.; Tsuno, Y.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1459.

cm$^{-1}$. MS $m/z$ 354 (M$^+$ 21), 338 (15), 57 (100).

**1,1-Bis[3-(*N*-oxy-*tert*-butylamino)phenyl]ethylene (*m,m′*-O′).** A mixture of 81.4 mg of 1,1-bis[3-(*N*-hydroxy-*tert*-butylamino)phenyl]ethylene, an excess amount (ca. 120 mg) of freshly prepared $Ag_2O$, and 3 mL of ether was stirred at 0 °C for 15 min and filtered with Celite. The filtrate was concentrated under reduced pressure at ambient temperature. After addition of a small amount of hexane, the residue was crystallized with hexane at −78 °C. After the supernatant was discarded, the *m,m′*-dinitroxide was obtained as orange thick oil. ESR ($CH_2Cl_2$, room temperature) $g = 2.0056$, $a_N = 6.3$ G (quintet). IR (neat) 798, 896, 1192, 1360, 1482, 1566, 1592, 2980 cm$^{-1}$. MS $m/z$: Calcd for $C_{22}H_{28}N_2O_2$: 352.2151. Found: 352.2151 (M$^+$, 0.5%), 337 (1.5%), 321 (4%), 57 (100%).

**Attempted Synthesis of 1,1-Bis[4-(*N*-oxy-*tert*-butylamino)phenyl]ethylene (*p,p′*-O′).** A mixture of 111 mg of 1,1-bis[4-(*N*-hydroxy-*tert*-butylamino)phenyl]ethylene, an excess amount (ca. 200 mg) of $Ag_2O$, and 10 mL of ether was stirred at room temperature for 10 min and filtered with Celite. After addition of hexane to the filtrate, the solvent was removed under reduced pressure at ambient temperature. The orange powder precipitate was collected. The product was insoluble in any ordinary organic solvent once isolated. Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01; N, 7.95. Found: C, 74.31; H, 7.93; N, 7.84. IR (KBr disk) 832, 1200, 1362, 1504, 1606, 2980 cm$^{-1}$.

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# Models for Intramolecular Exchange in Organic π-Conjugated Open-Shell Systems. A Comparison of 1,1-Ethenediyl and Carbonyl Linked Bis(arylnitrenes)

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**Abstract:** Linkage of two phenylnitrene electron-spin-bearing units by exchange coupling linker groups leads to model open-shell π-conjugated systems of the general structure :N–Ph–X–Ph–N: of various possible connectivity types. Use of variable-temperature electron spin resonance (ESR) spectroscopy of the dinitrenes with cross-conjugating linker groups –X– allowed study of the ground-state spin multiplicities of open-shell systems that are related in a connectivity sense to the theoretically important diradicals trimethylenemethane (–X– = >C=CH$_2$, 4,4′-connectivity), oxyallyl (–X– = >C=O, 4,4′-connectivity), and 1,1,2,3,3-pentamethylenepropane (–X– = >C=CH$_2$ or >C=O, 3,3′-connectivities). For 1,1-bis(4-nitrenophenyl)ethene, a quintet ground state was found with zero-field splitting parameters $|D/hc| = 0.151$ cm$^{-1}$ and $|E/hc| = 0.0029$ cm$^{-1}$. For the connectivity isomer (*E*)-3,4′-stilbenedinitrene, a quintet ground state with zfs parameters $|D/hc| = 0.146$ cm$^{-1}$, $|E/hc| = 0.0024$ cm$^{-1}$ was found. For 4,4′-dinitrenobenzophenone, a quintet ground state with zfs parameters $|D/hc| = 0.156$ cm$^{-1}$, $|E/hc| = 0.0046$ cm$^{-1}$, was found. For 1,1-bis(3-nitrenophenyl)ethene, a quintet state ESR spectrum was observed, with temperature-dependent intensity behavior that could be fit to a singlet < triplet < quintet states equilibrated model with a singlet ground-state, triplet at −28 cal/mol (−117 J/mol, a negative energy here signifying a low-spin singlet ground state), and quintet at −84 cal/mol (−351 J/mol). For 3,3′-benzophenonedinitrene, a quintet state spectrum was also observed, with temperature-dependent intensity behavior that could be fit by the same model with an ordering of states as follows: singlet ground state, triplet at −16 cal/mol (−67 J/mol), and quintet at −48 cal/mol (−201 J/mol). Overall, the results support the idea that minor heteroatom substitution (such as replacement of a 1,1-ethenediyl unit with a carbonyl unit) need not reverse qualitative connectivity-based exchange coupling effects. The dinitrenes that are disjoint are experimentally found to have low-spin ground states as predicted by the Borden–Davidson model (Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587), but in qualitative disagreement with some simple π-connectivity models (e.g.: Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297).

## Introduction

Chemists have long been interested in high-spin molecules. Recent advances in the observation of transient open-shell species has allowed study of numerous types of π-conjugated diradicals over the past 30 years. A particular incentive to study the electronic structure–property relationships of organic π-conjugated non-Kekulé molecules has been provided by theoretical suggestions that organic magnetic materials might be designed by rational design strategies that are based upon qualitative principles.[1-3] While it remains unclear whether practically useful materials will be realized from an intensive study of organic high-spin molecules, it is clear that successful strategies to design magnetic molecular materials from first principles will require a far more precise knowledge of intramolecular and intramolecular exchange interactions than is presently available.

Among the strategies presently being pursued for the design of molecular magnetic materials, one that has been pursued by our group (among several others) has been the idea of using structural linking moieties to couple together units bearing unpaired electron spin into a very high-spin molecule.[4,5] While bulk

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[‡] University of Massachusetts, Boston.

(1) Chiang, L. Y., Chaikin, P. M., Cowen, D. O., Eds. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 1.

(2) Dougherty, D. A.; Kaisaki, D. A. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 71.

(3) Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds. *Magnetic Molecular Materials*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; Vol. 198E.

(4) Lahti, P. M.; Ichimura, A. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 125.

(5) Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030.

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