4,6-Dimethoxy-1,3-phenylenebis(*N-tert*-butyl nitroxide) with a Singlet Ground State. Formal Violation of a Rule That *m*-Phenylene Serves as a Robust Ferromagnetic Coupling Unit

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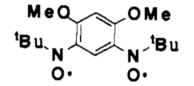
Abstract: 4,6-Dimethoxy-1,3-phenylenebis(*N-tert*-butyl nitroxide) (**1**) was prepared by lithiation of the corresponding dibromo compound followed by reaction with 2-methyl-2-nitrosopropane and subsequent treatment with Ag_2O. In a frozen toluene matrix, **1** showed EPR fine structures characteristic of triplet dinitroxides: $g = 2.0068$, $D/hc = 0.0179\ cm^{-1}$, and $E/hc = 0.0008\ cm^{-1}$. The variation in signal intensity vs reciprocal temperature deviated downward from a Curie relationship at temperatures lower than 45 K, suggesting a singlet ground state for **1**. The effective magnetic moment obtained on a Faraday balance and a SQUID susceptometer showed a limiting value of 2.45 μ_B at higher temperatures, a value consistent with degenerate singlet and triplet states. The temperature dependence for a sample of **1** in PVC film revealed a weak antiferromagnetic coupling, $2J/k_B = -7.0$ K, whereas the coupling was strongly antiferromagnetic for crystalline samples: $2J/k_B = -73.8$ K. An X-ray structure analysis of an orange-colored monoclinic single crystal of **1**, $P2_1$ (No. 4), $a = 9.8914$ (8) Å, $b = 7.904$ (3) Å, $c = 11.4547$ (6) Å, $\beta = 106.258$ (5)°, $V = 859.8$ (3) $Å^3$, $Z = 2$, revealed the molecular structure **1b** with two nitroxide groups out of the plane of the phenylene ring by 65.1° and 75.3° in a syn conformation. There is no interradical distance closer than 7.0 Å between neighboring molecules. Lower spin polarization on the *m*-phenylene ring and a possible antiferromagnetic through-space interaction may be responsible for the nonferromagnetic coupling in **1**.

π-Conjugated polyradicals with a high-spin ground state are designed on the basis of the idea that the electron spins of a pair of radical centers can be aligned in parallel when these centers are connected through an appropriate ferromagnetic coupling unit.[1] Out of a number of such couplers, *m*-phenylene has been established to be the most dependable. Not only carbon- and nitrogen-centered radicals in doublet states[2,3] and trimethylenemethane,[4] carbenes,[5] and nitrenes[5b,6] in triplet states but also polarons[7] have been shown to couple ferromagnetically when connected through this coupling unit. By repeating such a fragment, which consolidates the spin and ferromagnetic coupler to form one- or two-dimensional arrays of ordered spins in oligomers and polymers, high-spin organic molecules with unprecedentedly large magnetic moments have been constructed.[8]

The *m*-phenylene coupler has successfully been modified to the 5-*tert*-butyl,[3e] 5-octadecyloxy,[7] 4,6-dimethyl, 4,6-diisopropyl, 2,4,6-trimethyl,[9,10] and tetrachloro derivatives,[11] showing that it is an extremely versatile ferromagnetic coupling unit. In view of such a central role played by the *m*-phenylenes as ferromagnetic coupling units for the design of magnetic organic materials, any limitation on their performance in this capacity is worth knowing. *p*-Methoxyphenyl nitroxides are known to be more persistent than the parent phenyl nitroxides.[12] A naive extension led us to assume that a similar kinetic/thermodynamic stabilization of diradicals would be effected by a 4,6-dimethoxy-*m*-phenylene unit in dinitroxide **1**. This assumption has proved to be incorrect in this study.



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Results

Synthesis of the Dinitroxide. 1,3-Dibromo-4,6-dimethoxybenzene[13] was dilithiated with 2 equiv of *n*-butyllithium in anhydrous ether. The mixture was allowed to react with 2.2 equiv of 2-methyl-2-nitrosopropane at −78 °C to give 1,3-bis(*N-tert*-butyl-*N*-hydroxyamino)-4,6-dimethoxybenzene, which was then treated with Ag_2O. The solid thus obtained was recrystallized from ether to give **1** as analytically pure orange needles, mp 148 °C.

EPR Spectra. The EPR spectra of **1** in fluid solutions (3×10^{-4} M) at room temperature were unusual for a diradical (Figure 1). They appeared to be an overlap of two types of spectra: a broad singlet with a peak-to-peak width of 36.0 G and a set of three narrower lines exhibiting hyperfine coupling with a nitrogen nucleus ($a_N = 14.2$ G). The latter is too strong (≤40%) to be assigned to an adventitious monoradical. The presence of two conformers, *anti*-**1a** and *syn*-**1b**, is suggested as a possible ex-

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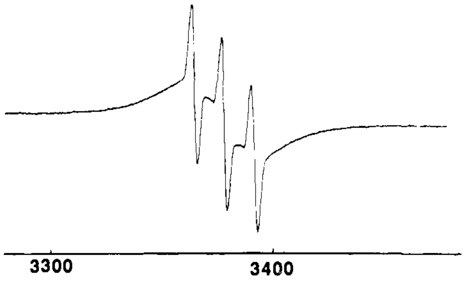


Figure 1. X-band EPR spectrum (9.49 GHz) obtained for a solution of **1** in toluene at 23 °C.

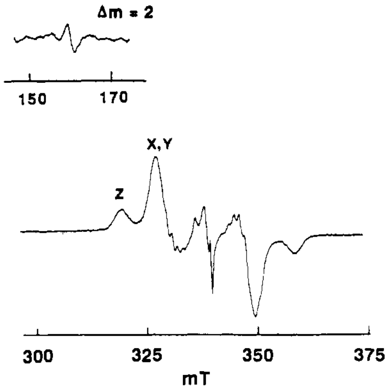
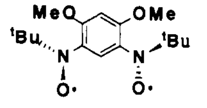
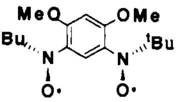


Figure 2. X-band EPR spectra (9.49 GHz) obtained for a solution of **1** in toluene at 17 K.

planation for the spectra. The proportion of the sharp signals relative to the broad one decreased in 2-methyltetrahydrofuran and dichloromethane, solvents having higher dielectric constants.



1a



1b

In a 10^{-3} M toluene rigid glass, **1** showed an X-band EPR fine structure typical of a dinitroxide in a triplet state[3] (Figure 2; $g_{av} = 2.0068$, $D/hc = 0.0179$, and $E/hc = 0.0008$ cm^{-1}). A $\Delta m_s = 2$ transition was observed at 169.2 mT. A plot of the variation in signal intensity due to the triplet dinitroxide vs reciprocal temperature followed the Curie law in the range 45–120 K. At lower temperatures, the plot deviated from the linear relationship and became slightly convex, showing that the ground state is most likely a singlet state. Since it was difficult to avoid saturation of the signal intensity at the lower temperature despite the application of a lower microwave power and modulation, an estimation of the energy gap by fitting the EPR intensity data to a Bleaney–Bowers-type equation (eq 1)[14] was not made. Aside from these signals, a broad plus/minus peak with some structures was observed at $g = 2$ (Figure 2).

$$\chi = \frac{2Ng^2\mu_B}{kT[3 + \exp(-2J/kT)]} \qquad (1)$$

Magnetic Susceptibility. The magnetic susceptibility, χ, of a diluted sample of **1** (2 mol %) in poly(vinyl chloride) (PVC) was determined on a Faraday balance at a magnetic field strength of 2.0 T. The data are expressed as the plot of effective magnetic moment μ_{eff} vs temperature in Figure 3. As the temperature was increased, the μ_{eff} value increased slightly at first but leveled off at ca. 2.45 μ_B over the range 45–300 K. The results are interpreted in terms of nearly degenerate triplet and singlet states. The χ values were simulated by a Bleaney–Bowers equation (eq 1)[14] in which $2J = -7.0k_B$ K = -4.9 cm^{-1}. Hence, the observed triplet lies slightly above the ground singlet state.

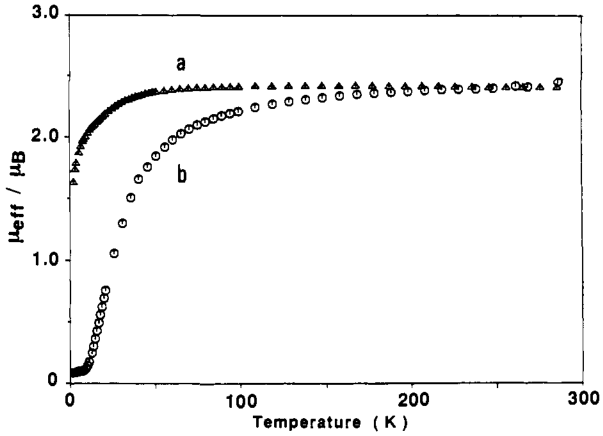


Figure 3. Temperature dependence of μ_{eff} values of **1** in (a) PVC films and (b) neat crystals.

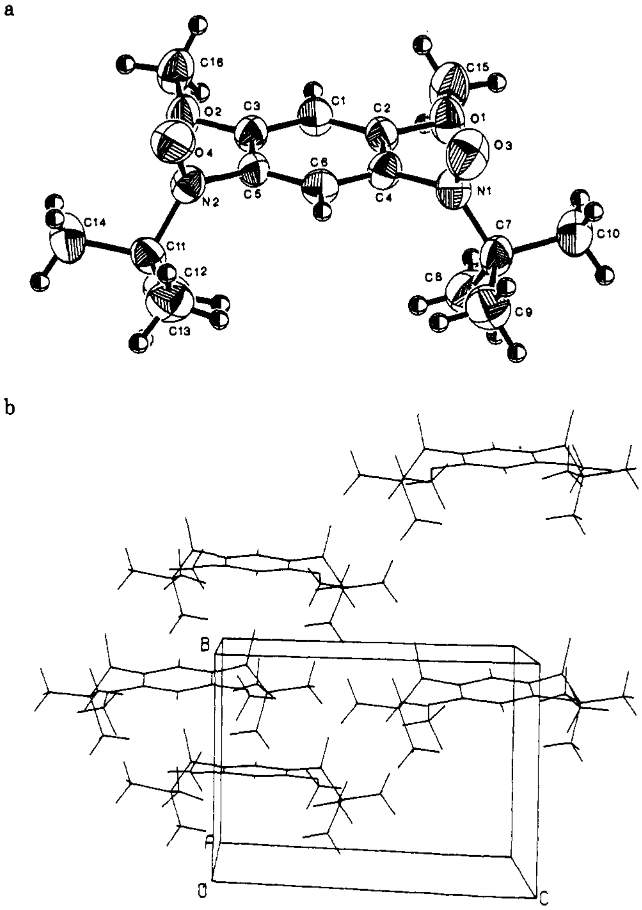


Figure 4. (a) Molecular and (b) X-ray crystal structures of **1**.

Similar experiments for a microcrystalline sample of **1** have been performed on a Faraday balance at a magnetic field strength of 2.0 T and on a SQUID susceptometer/magnetometer at 0.5 T. The data from the two measurements were indistinguishable. The effective magnetic moments were dominated by antiferromagnetic interactions; as the temperature was raised from 2 K, μ_{eff} increased sharply up to ca. 50 K and then increased more gradually to a limiting value of 2.45 μ_B (Figure 3). The data were analyzed in terms of a singlet/triplet model in which $2J = -73.8k_B$ K = -51.3 cm^{-1}; the ground state is decidedly a singlet state.

X-ray Crystal Structure Analysis. An X-ray crystal structure analysis was carried out on a monoclinic single crystal ($P2_1$ (No. 4)) of **1**: $a = 9.8914$ (8) Å, $b = 7.904$ (3) Å, $c = 11.4547$ (6) Å, $\beta = 106.258$ (5)°, $V = 859.8$ (3) Å^3, and $Z = 2$. While the two methoxyl groups are nearly ($\leq 10°$) in the same plane as the

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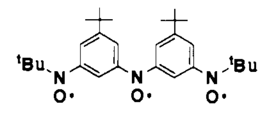
m-phenylene unit, the *tert*-butyl nitroxide moieties are considerably out of this plane (by 65.1° and 75.3°) and in syn conformation **1b** (Figure 4a). The distances between the two nitroxide moieties within a molecule are $r(NN') = 5.42$ Å, $r(OO') = 6.06$ Å, and $r(\overline{NON'O'}) = 5.74$ Å. There are no intermolecular distances shorter than 7.04 Å between any pair of atoms involved in adjacent nitroxide radicals. There are no signs of the formation of a dimer, either (Figure 4b).

Discussion

It has been accepted that the *m*-phenylenes are extremely versatile ferromagnetic coupling units. In general, how strongly does the *m*-phenylene coupler align doublet and triplet spins attached to its two ends? Since the higher spin states are the ground states and the lower spin states cannot often be populated thermally, it is not possible to determine from a simple Boltzmann distribution how strongly the two open-shell centers interact through this ferromagnetic coupling unit. Kato et al. performed an ab initio study on *m*-benzoquinodimethane and found that the singlet is less stable than the triplet by 10.1 kcal/mol (~0.44 eV).[15a] Another theoretical calculation placed the singlet higher in energy than the ground triplet state by $2J = 0.2$ eV.[15b] It is only persistent trinitroxide **2** in which the effective magnetic moments were measured over a temperature range of 300 K, allowing the determination of the exchange integral between the neighboring nitroxides as $J = 167$ cm^{-1}.[3e] The discrepancy of this value from the theoretical ones by an order of magnitude has been ascribed to the more localized spins of the nitroxide radicals and the consequent smaller polarization of the π-electrons on the phenylene rings. Whereas the trinitroxide is kinetically stabilized by steric protection, a similar kinetic/thermodynamic stabilization has now been sought by introducing methoxyl groups on the *m*-phenylene unit.



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It is usually the case that no EPR signal is observable or only a broad signal is observed for triplet species in solution, since the spin–lattice relaxation time τ_c is very short due to efficient dipole–dipole interaction under these conditions. A ca. 30 G wide single line has been shown to correspond to a τ_c value of 4×10^{-11} s.[16] When a D value is very small, a typical EPR spectrum due to rapidly tumbling radicals might become observable. The presence of two conformers, *anti*-**1a** and *syn*-**1b**, is suggested as a possible explanation for the spectra of **1** that show overlaps of the two kinds of signals. Actually, the proportion of sharp signals relative to the broad one decreased in more polar solvents. Since **1b** has the two terminal oxygen atoms of its nitroxide radicals in closer proximity than does **1a**, the former should have a meaningful D value (vide infra), a consequent shorter τ_c, and a broader signal. On the other hand, the radical centers in **1a** are farther apart and the dipolar relaxation should not be extremely fast. The hyperfine coupling with one nitrogen nucleus rather than two suggests that $J \ll a_N$ in this conformer.

In rigid glasses, typical fine structures characteristic of a triplet dinitroxide have been obtained for **1**. The observed D/hc value of 0.0179 cm^{-1} (=191.0 G) corresponds to an interradical distance of 5.26 Å when $D/G = 27810/r^3$ is assumed under the point dipole approximation.[17] This value is in good agreement with those observed for **1b** in crystals. A broad ± signal at $g =$ ca. 2 may be assigned to the other conformation with very small zfs values.

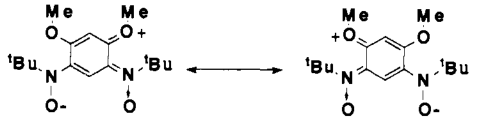
Most unexpected was the temperature dependence of the effective magnetic moments, μ_{eff} (Figure 3), measured on a Faraday balance and a SQUID susceptometer. As the temperature was raised from 2 K, μ_{eff} increased sharply and reached a plateau at ca. 50 K, but increased steadily to approach a value of 2.45 μ_B at 300 K. The observed limiting value is consistent with degenerate triplet and singlet states. Therefore, the increase in the intermediate temperature range is interpreted in terms of a thermal population of the triplet state and can be simulated by a Bleaney–Bowers equation (eq 1)[14] in which $2J = -51.3$ cm^{-1}. A species with a ground triplet state should have given a μ_{eff} value of 2.83 μ_B.

According to the singlet/triplet model described by eq 1, μ_{eff} should be 0 at 0 K. The observed small nonzero μ_{eff} value of the crystalline samples might be ascribed to population of the lowest spin sublevel of the excited triplet due to Zeeman splitting, which could appear below the ground singlet. The latter possibility is ruled out since the Zeeman splitting is established to amount to only 0.5 cm^{-1} at 0.5 T from the observed zfs values, while the energy gap between the two states is 51.3 cm^{-1}, 2 orders of magnitude greater than the former. Contamination of **1** with ca. 4% adventitious mononitroxide is enough to explain the nonzero μ_{eff} value.

It is often the case that μ_{eff} values of free radicals in neat crystals decrease at lower temperatures because of antiferromagnetic interradical exchange coupling. Transitions into diamagnetic dimers are sometimes observed in the extreme.[18] The X-ray crystal structure, although taken at room temperature, is not compatible with such interradical interaction. Therefore, it is highly likely that the strong antiferromagnetic coupling is intramolecular. The effective magnetic moment data in PVC are consistent with this interpretation; even when **1** was diluted (2 mol %) to exclude the intermolecular exchange coupling between the diradical molecules, the two spins were weakly coupled in an antiferromagnetic fashion. The apparent weakened coupling is probably due to the population of the other conformer(s) having weaker antiferromagnetic coupling.

Ferromagnetic coupling through the *m*-phenylene unit is induced by alternate polarization of the π-spins on the phenylene ring. It is well-established that the electron spins are more localized at the N–O bond and that the phenyl ring carries only a fraction of the spin density in phenyl nitroxides.[19] Furthermore, the nitroxide moieties are not coplanar with the phenylene ring in **1**: the dihedral angles are as large as 65.1° and 75.3°, making the spin polarization on the ring even smaller. Under these circumstances, the through-space exchange interaction between the two nitroxide units 5.4 Å apart at the two nitrogen atoms on the same phenylene ring may not be negligible. Since the spins of same sign face each other,[20] this interaction of the two nitroxides may be antiferromagnetic. A recent APUHF STO-3G calculation suggested that such a face-to-face interaction would be antiferromagnetic and would amount to the effective exchange integral of -39.5 cm^{-1} when the nitroxides are placed in parallel 3.0 Å apart but not canted as in **1b**.[20e]

Alternatively, the observed singlet ground state might be considered to arise from stabilization of this state by resonance, i.e., by contribution of resonance structures **3**. However, the X-ray crystal structure shows that the nitroxide moieties are almost



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perpendicular to the phenylene plane, and there is no sign of shortening of the bonds connecting the nitrogen and oxygen atoms with the phenylene ring (1.49 and 1.41 Å, respectively, values typical of anisoles and phenyl nitroxides).[21] The C–C bond lengths of the *m*-phenylene ring are within 1.36–1.39 Å. Thus, the possibility of **3** is discounted.

Conclusion

The 4,6-dimethoxy-*m*-phenylene unit in **1** is not a ferromagnetic coupling unit; the two nitroxide groups couple in an antiferromagnetic fashion strongly in crystals and weakly in solid solutions. Lower π-spin polarization on the *m*-phenylene ring and a possible antiferromagnetic through-space interaction between the spins rather localized on the nitroxide radicals at a distance of 5.74 Å (between the two middle points of the N–O bonds) in conformation **1b** may be responsible for the nonferromagnetic coupling in **1**.[22] In toluene and PVC solid solutions, **1** is presumed to take other conformations,[10] e.g., a more planar conformation, or the anti form **1a**, in which the antiferromagnetic coupling is less effective. Much care should be taken in the proper choice of a combination of spins and ferromagnetic couplers for designing high-spin polymers.

Experimental Section

EPR Spectroscopy and Magnetic Measurements. EPR spectra were recorded by using a Bruker ESP 300 X-band (9.4 GHz) spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter. An Air Products LTD-3-110 liquid helium transfer system was attached for the low-temperature measurements. The magnetic susceptibility was measured by the Faraday balance method at 2 T on an Oxford Instruments magnetic susceptibility system with a 7-T superconducting solenoid as described previously.[3e] A quantum design SQUID susceptometer/magnetometer was also used for a microcrystalline sample. Accurately measured ca. 15 mg samples of **1** and main fields of 2 and 0.5 T were used for the balance and SQUID measurements, respectively.

X-ray Analysis. A single crystal of approximate dimensions 0.02625 mm^3 was mounted on a glass fiber support. Diffraction data were obtained on a Rigaku AFC-5R four-circle diffractometer with $2q(\max) = 55.1°$ using graphite-monochromated Mo Kα radiation (2.64 cm^{-1}) at 23 °C. The structure was solved in $P2_1$ (No. 4) by direct methods and converged by full-matrix least-squares analysis using the TEXSAN Version 2.0 program (Molecular Structure Corporation). Crystal data were as follows: $C_{16}H_{26}N_2O_4$, $M = 310.39$, monoclinic, space group $P2_1$ (No. 4), $a = 9.8914\ (8)$ Å, $b = 7.904\ (3)$ Å, $c = 11.4547\ (6)$ Å, $\beta = 106.258\ (5)°$, $V = 859.8\ (3)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.199$ g cm^{-3}. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at standard positions (C–H = 0.96 Å; C–C–H = 109.5°, 120°, or 180°) and refined isotropically using a rigid model. Refinement converged at $R = 0.040$ and $R_w = 0.041$ for 1153 unique reflections with $I > 3\sigma(I)$ and 198 variables.

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.

Materials. Solvents diethyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, benzene, and toluene that were used for the reactions and spectral measurements were all distilled under high-purity N_2 after they were dried with sodium/benzophenone ketyl. All reaction mixtures were stirred under an atmosphere of N_2. Anhydrous magnesium sulfate was used as drying agent.

4,6-Dimethoxy-1,3-phenylenebis(*N*-*tert*-butyl-*N*-hydroxyamine). To a solution of 1.48 g (5.0 mmol) of 1,3-dibromo-4,6-dimethoxybenzene[14] in 75 mL of anhydrous ether was added 6.3 mL (10.0 mmol) of 1.6 M *n*-butyllithium in hexane at −78 °C. The mixture was allowed to warm up to ambient temperature, after which 0.97 g (11.0 mmol) of 2-methyl-2-nitrosopropane in 10 mL of ether was added at −78 °C. The mixture was stirred overnight at room temperature and then decomposed with aqueous ammonium chloride. Column chromatography on silica gel (Wako Gel C 200) gave 0.66 g (42%) of bis(hydroxyamine) as a colorless solid: ^{1}H NMR (CDCl$_3$) δ 1.18 (s, 18 H), 3.83 (s, 6 H), 5.73 (br, 2 H), 6.36 (s, 1 H), 7.55 (s, 1 H).

4,6-Dimethoxy-1,3-phenylenebis(*N*-*tert*-butyl nitroxide). A solution of 0.50 g of the bis(hydroxyamine) in 20 mL of ether was treated with 3 equiv of freshly prepared Ag$_2$O. The red solids thus obtained were recrystallized from ether to give red needles. Anal. Calcd for $C_{16}H_{26}N_2O_4$: C, 61.94; H, 8.39; N, 9.03. Found: C, 61.73; H, 8.27; N, 8.94.

Acknowledgment. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 03102003) from the Ministry of Education, Science and Culture.

Supplementary Material Available: Thermal ellipsoid plot and tables of crystal and intensity collection data, atomic coordinates, torsion angles, and anisotropic displacement parameters for **1** (6 pages); tables of observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

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(22) The results obtained in this paper, namely, that the 4,6-dimethoxy-*m*-phenylene unit is not a ferromagnetic coupling unit at least for *tert*-butyl nitroxides, and perhaps in general, are quite in contrast with those for other congested *m*-phenylene couplers reported in the literature.[9,11] It is surprising that the triarylmethyl-type diradicals containing 4,6-dimethyl-, 4,6-diisopropyl-, and 2,4,6-trimethyl-*m*-phenylene couplers[9] all have triplet ground states. The observed μ_{eff} values of 2.2, 2.5, and 2.2 μ_B, respectively, for these diradicals are considerably lower than the 2.83-μ_B value of ground-state triplets and would require purities of the samples of only 79, 89, and 79%, respectively. These reported data might alternatively be regarded as being closer to the 2.45-μ_{eff} value expected for diradicals in nearly degenerate singlet/triplet states.

Efficient Pyrimidine Dimer Radical Anion Splitting in Low Polarity Solvents

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Received June 11, 1992

Abstract: Photosensitized pyrimidine dimer splitting by a covalently linked methoxybenzene exhibited a strong solvent dependence. Fluorescence of the chromophore was quenched by the attached dimer, which was indicative of electron transfer from excited chromophore to dimer. The quantum efficiency of splitting of the dimer radical anion in the linked dimer$^{\bullet-}$–chromophore$^{\bullet+}$ was calculated from the observed quantum yields of splitting and the degree of fluorescence quenching. The quantum efficiency of dimer radical anion splitting was remarkably dependent on solvent polarity, ranging from 0.05 in water to ~0.5 in low polarity solvent mixtures (e.g., heptane/1,4-dioxane, 95:5). The results were rationalized in terms of competition of splitting and back electron transfer within the charge-separated species. The latter pathway may be slowed due to its exergonicity in low polarity media, in accord with Marcus inverted behavior. Photolyases may be effective for splitting dimers by providing catalytic groups and a medium in which both dimer radical anion formation and splitting are efficient.

DNA repair has received heightened attention in recent years as ozone depletion threatens to significantly increase DNA damage by UV-B radiation (280–320 nm). Among the major lesions formed in DNA by this radiation are pyrimidine dimers (cyclo-

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