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Ab Initio Calculations Show Why *m*-Phenylene Is Not Always a Ferromagnetic Coupler

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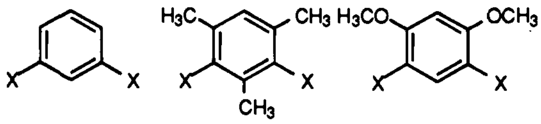
Abstract: In agreement with the experimental results of the groups of Rassat and Iwamura on respectively *m*-phenylene bis(*tert*-butyl nitroxides) **2** and **3**, *ab initio* calculations on *m*-benzoquinodimethane (**1a**) and *m*-phenylene bis(nitroxide) (**1d**) find that near dihedral angles of $\phi = 90°$ between the benzene ring and the radical-bearing groups, the singlet falls below the triplet in energy. The change in *m*-phenylene from a ferromagnetic coupler at angles around $\phi = 0°$ to an antiferromagnetic coupler around $\phi = 90°$ is found to be largely due to selective destabilization of the antisymmetric (A) combination of the singly-occupied orbitals on each of the radical centers by a σ orbital of this symmetry on the *m*-phenylene coupler. The asymmetry about $\phi = 90°$ in the singlet–triplet energy difference that is calculated for **1d** is shown to be due to additional interactions of the oxygens of the singly-occupied nitroxyl orbitals with p–π AOs of the benzene ring.

When two groups, X, each bearing a single electron in a π orbital, are linked by *m*-phenylene as in **1**, the two π electrons are almost invariably coupled ferromagnetically.[1,2] *m*-Phenylene acts as a robust ferromagnetic coupler for the spins of the π electrons, not only on a pair of carbon-centered radicals (**1a**),[3] but also on two carbenes (**1b**),[4] on nitrogen in aza analogs of **1a** and **b**,[5] and on two *tert*-butylnitroxyl groups (**1c**).[6] A pair of 2-methylenecyclopentane-1,3-diyls[7] and two polarons[8] have also been found to be coupled ferromagnetically by *m*-phenylene.

It is particularly noteworthy, therefore, that two *m*-phenylene bis(*tert*-butyl nitroxides), **2**[9] and **3**,[10] have each been found to have a singlet, rather than a triplet, ground state. Rassat[9] and Iwamura[10] both suggested that the antiferromagnetic coupling of the spins in respectively **2** and **3** might be related to the geometries of these molecules. Rassat and co-workers speculated that the methyls in **2** cause the *tert*-butylnitroxyl groups to be twisted out of conjugation with the *m*-phenylene linker; and two isomers (presumably with *syn* and *anti* *tert*-butylnitroxyl groups) of **2** were, in fact, isolated.[9] Iwamura and co-workers obtained an X-ray structure of **3** in which the dihedral angles between the crystallographically non-equivalent *tert*-butylnitroxyl groups and the plane of the benzene ring were found to be 65° and 75°.[10]



1a, X = $\dot{C}H_2$
b, X = $\ddot{C}Ph$
c, X = $(CH_3)_3CN(\dot{O})$
d, X = $HN(\dot{O})$

2, X = $(CH_3)_3CN(\dot{O})$

3, X = $(CH_3)_3CN(\dot{O})$

To the extent that the *tert*-butylnitroxyl groups are twisted out of conjugation with the *m*-phenylene linker, the ability of *m*-phenylene to couple the nitroxyl spins ferromagnetically should be reduced. However, the mechanism by which the spin coupling becomes antiferromagnetic, so that the singlet falls below the triplet in both **2** and **3**, remains unclear. The distance between the nitroxyl groups in **2** and **3** is sufficiently large (>5 Å)[10] that a significant through-space, bonding interaction between them seems highly unlikely. Moreover, although the majority of the spin density in a nitroxyl group resides on oxygen, the *syn* and *anti* isomers of **2** were found to have comparable singlet–triplet splittings.[9] This finding provides experimental evidence against long-range bonding between the nitroxyls being responsible for the antiferromagnetic spin coupling observed in **2**.

In order to try to understand why *m*-phenylene acts as an antiferromagnetic, rather than ferromagnetic, coupler in **2** and **3**, we have performed *ab initio* calculations on *m*-phenylene bis(nitroxide) **1d** at nonplanar C_s (*syn*) and C_2 (*anti*) geometries. We find that around dihedral angles of 90° between the nitroxyl groups and the *m*-phenylene linker, the singlet falls below the triplet in energy in both isomers. Our calculations reveal that

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[1] In the field of molecular magnetism electron spins with a preferred parallel orientation are said to be coupled "ferromagnetically", despite the fact that a single molecule cannot be a ferromagnet. See, for example: Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

[2] This can be explained, using either MO theory (Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587) or valence-bond arguments (Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297). These two theoretical approaches have been compared and contrasted (Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 1–72. Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195).

[3] (a) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628. (b) Using the benzoquinodimethane (**1a**) motif, it has been possible to prepare a variety of polyradicals in which the spin coupling is ferromagnetic. Review: Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

[4] (a) Itoh, K. *Chem. Phys. Lett.* *1967*, *1*, 235. Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzollo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. (b) Polycarbenes of this type, with all the carbenic centers coupled ferromagnetically, have also been prepared. Reviews: Iwamura, H. *Pure Appl. Chem.* **1986**, *58*, 197. Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

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[9] Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180.

[10] Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.

Table 1. Relative GVB and ROHF/6-31G* Energies (kcal/mol)[a] of the Lowest Singlet and Triplet States in the *syn* (C_s symmetry) and *anti* (C_2 symmetry) Conformations of *m*-Phenylene Bis(nitroxide) (**1d**) as a Function of Dihedral Angle (ϕ) between the Nitroxyl Groups and the Benzene Ring[b]

	syn nitroxyls			*anti* nitroxyls		
ϕ (deg)	$^1A'$	$^3A''$	$^1A'-^3A''$	^1A	^3B	$^1A-^3B$
0	0.28	0	0.28	0.28	0	0.28
15	1.22	0.97	0.25	1.20	0.94	0.26
30	3.74	3.56	0.18	3.66	3.47	0.19
45	7.06	6.97	0.09	6.85	6.78	0.07
60	10.23	10.20	0.03	9.86	9.87	−0.01
75	12.42	12.42	0.00	11.93	11.97	−0.04
90	13.15	13.18	−0.03	12.64	12.66	−0.02
105	12.29	12.34	−0.05	11.88	11.88	0.00
120	10.05	10.08	−0.03	9.79	9.76	0.03
135	6.96	6.88	0.08	6.82	6.74	0.08
150	3.82	3.62	0.20	3.76	3.59	0.18
165	1.48	1.22	0.26	1.46	1.22	0.24
180	0.61	0.35	0.26	0.61	0.35	0.26

[a] Relative to $E = -489.168\,373$ hartrees. [b] $\phi = 0°$ corresponds to the N−O bonds and the C−H bond at C-2 being *syn*.

the singlet becomes the ground state of **1d**, not because of a through-space interaction between the nitroxyls but because the σ bonds of the *m*-phenylene group selectively destabilize the out-of-phase combination of singly-occupied orbitals on the twisted nitroxyl groups. The singlet is calculated to fall farthest below the triplet in energy at geometries in which the energy difference between the in-phase and out-of-phase combinations of these nitroxyl orbitals is increased by interactions between the nitroxyl oxygens and the p−π AOs of the benzene ring.

Computational Methodology

The geometries of the lowest singlet and triplet state of **1d** were optimized at a series of C_s and C_2 geometries with the dihedral angle, ϕ, between the nitroxyl groups and the benzene ring fixed. Calculations were performed with the 6-31G* basis set,[11] using GVB wave functions for the singlet and ROHF wave functions for the triplet. The optimized geometries of the two states, which are available as supporting information,[12] were very similar and showed only small variations with ϕ.

In order to explore further the effect of dihedral angle on the ability of *m*-phenylene to serve as a ferromagnetic coupler, calculations were also carried out on *m*-benzoquinodimethane (**1a**). The smaller size of this diradical made it possible to perform not only GVB-ROHF but also CASSCF calculations on it. These calculations included all configurations that arise when eight electrons are allowed to occupy eight orbitals. These (8/8) CASSCF calculations were carried out at the GVB and ROHF optimized geometries. All calculations were performed with the Gaussian 92 suite of *ab initio* programs.[13]

Results and Discussion

The effect of ϕ on the GVB energy of the singlet state of **1d** and the ROHF energy of the triplet state is given in Table 1, and the singlet−triplet energy difference ($2J$) as a function of ϕ is shown graphically in Figure 1. Calculations at the GVB-ROHF level would not be expected to give quantitatively accurate values for either the rotational barrier heights or the energy differences between the singlet and triplet.[14] However, there is no reason to doubt the correctness of the qualitative result, that the ground state changes from a triplet for values of ϕ around 0° (nitroxyl oxygens *cisoid* to the unique hydrogen at C-2) and 180° (nitroxyl oxygens *transoid* to this hydrogen) to a singlet for values of ϕ around 90°.

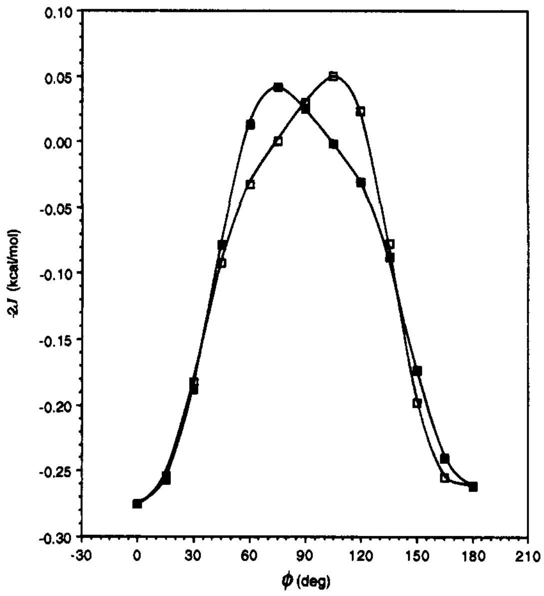

Figure 1. Plots of $-2J$ [$-E(^1A'-^3A'')$ for *syn* nitroxyls (□) and $-E(^1A-^3B)$ for *anti* nitroxyls (■)] in **1d** versus dihedral angle (ϕ).

Table 2. Relative GVB, ROHF, and (8/8) CASSCF/6-31G* Energies (kcal/mol) of the Lowest Singlet and Triplet States of *m*-Benzoquinodimethane (**1a**) at Dihedral Angles (ϕ) between the Methylene Groups and the Benzene Ring of $\phi = 0°$ and 90°

	GVB-ROHF			(8/8) CASSCF		
ϕ (deg)	$^1A_1$	$^3B_2$	$^1A_1-^3B_2$	$^1A_1$	$^3B_2$	$^1A_1-^3B_2$
0	2.75	0[a]	2.75	10.76	0[b]	10.76
90	14.43	14.69	−0.26	23.71	23.89	−0.18

[a] Relative to $E = -307.527\,037$ hartrees. [b] Relative to $E = -307.614\,253$ hartrees.

As shown in Figure 1, the singlet lies farthest below the triplet ($-2J > 0$) at $\phi > 90°$ when the nitroxyl groups are *syn* and at $\phi < 90°$ when they are *anti*. For a radical center, X, with an axis of symmetry (e.g., planar $CH_2^{\bullet}$), geometries with $\phi < 90°$ are indistinguishable from geometries with $\phi > 90°$; so energies must be symmetrical about $\phi = 90°$. Therefore, the distinct differences, shown in Figure 1, between the singlet−triplet energy differences at $\phi < 90°$ and $\phi > 90°$ are attributable to the asymmetry of the nitroxyl group and, in particular, to the fact that the oxygen atom in it carries most of the spin.[15]

In order to establish whether the change around $\phi = 90°$ of *m*-phenylene from a ferromagnetic to a antiferromagnetic coupler is restricted to the coupling of the electron spins on nitroxyl groups, we also carried out calculations on *m*-benzoquinodimethane (**1a**). In agreement with experiment,[3a] previous calculations have found *m*-phenylene to be a very strong ferromagnetic coupler in the planar diradical;[14] but calculations have not been performed at geometries of **1a** in which the methylene groups are twisted out of conjugation with the *m*-phenylene linker.

The results of our GVB-ROHF and CASSCF calculations on **1a** are given in Table 2. As found for **1d**, the singlet is calculated to lie below the triplet at $\phi = 90°$. Unlike the case in **1d**, the unpaired spins in **1a** are concentrated on the atoms

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(11) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(12) Ordering information is given on any current masthead page.

(13) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc.: Pittsburgh, PA, 1992.

(14) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791. Fort, R. C., Jr.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549.

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

directly attached to the *m*-phenylene linker. Consequently, the GVB-ROHF rotational barriers in **1a** are larger than those in **1d**; and at both $\phi = 0°$ and 90° the magnitudes of the GVB-ROHF energy differences between the singlet and the triplet are also larger.

As discussed elsewhere,[14] the additional electron correlation provided at the (8/8) CASSCF level for planar **1a** selectively stabilizes the more delocalized triplet state. On going from ROHF to the CASSCF level the barrier to rotation of both methylene groups in the triplet increases by 9.20 kcal/mol. For the more localized planar singlet, correlating all eight π electrons provides little additional stabilization; so the CASSCF barrier of 12.95 kcal/mol to rotation of both methylene groups exceeeds the GVB barrier by only 1.27 kcal/mol.

The increase of 7.93 kcal/mol in the difference between the rotational barriers for the two states is nearly the same as the 8.01 kcal/mol increase in the adiabatic singlet−triplet energy difference. The small difference between these two increases is due to the fact that, at the $\phi = 90°$ transition states for simultaneous methylene rotations, the singlet drops below the triplet by 0.08 kcal/mol less at the CASSCF level than at ROHF/GVB. On going from ROHF/GVB to CASSCF, the change in the singlet−triplet splitting at $\phi = 90°$ is small, since the additional six electrons that are correlated at the CASSCF level are in π orbitals that are orthogonal to the MOs that contain the two nonbonding electrons.

In order to assess the effect of also including correlation among the σ electrons in **1a** at $\phi = 90°$, we performed CASPT2N calculations, which use second-order perturbation theory to correlate those electrons that are not correlated in the reference wave function.[16,17] Starting from the GVB and ROHF wave functions for respectively the singlet and the triplet, the CASPT2N value for the energy difference between these two states is 0.07 kcal/mol larger than the GVB-ROHF value. It would appear, therefore, that GVB-ROHF calculations probably underestimate slightly the stability of the singlet, relative to the triplet, around $\phi = 90°$ in **1a** and, by inference, in **1d** too.

The change from a triplet to a singlet ground state that is calculated to occur in both **1a** and **1d** at values of ϕ around 90° cannot be due to long-range bonding between the radical centers through space. This was established for both diradicals by GVB-ROHF calculations, performed at the optimized $\phi = 90°$ geometry after excising the *m*-phenylene linker and replacing it with two hydrogen atoms, one attached to each $HNO^•$ or $CH_2^•$ group. For both the $H_2NO^•$ and the $CH_3^•$ radical pairs, the singlet and triplet were computed to have the same energy to within 0.01 kcal/mol.[18]

Since through-space interactions cannot be responsible for the singlet ground states computed for **1a** and **1d** at values of ϕ around 90°, clearly the singlet states must be stabilized, relative to the triplets, by through-bond interactions.[19] The radical centers interact with the central two of the four σ bonds that connect them. The antisymmetric (A) combination of the singly occupied orbitals at each radical center interacts with the A combinations of the σ and σ^* orbitals. To these ring orbitals C-2 contributes only the 2p AO that is directed toward the radical centers. This 2p AO mixes in an antibonding fashion with the A combination of the orbitals at the radical centers. This is shown in Figure 2,[20] which depicts the resulting A nonbonding (NB)MO in **1a** at $\phi = 90°$.

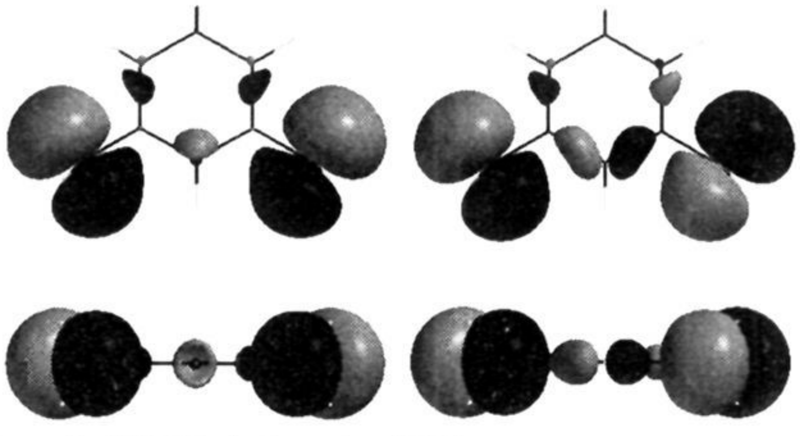

Figure 2. NBMOs in **1a** at $\phi = 90°$.[20]

The symmetric (S) combination of singly occupied orbitals interacts with the S combinations of the σ and σ^* ring orbitals, to which C-2 contributes its 2s AO, as well as the 2p AO that is oriented along the bond to the hydrogen. The resulting S NBMO in **1a** at $\phi = 90°$ is also shown in Figure 2.

Because of the large amount of 2s character and the orientation of the 2p AO at C-2 in the S combination of σ and σ^* orbitals, their mixing with the orbitals at the radical centers destabilizes the resulting S NBMO less than the mixing of the A combination of σ and σ^* orbitals with the orbitals at the radical centers destabilizes the A NBMO. Therefore, as expected for an interaction which involves radical centers that are connected by four bonds,[19] in both **1a** and **1d** the S NBMO lies below the A NBMO at $\phi = 90°$. This lifting of the degeneracy of the S and A combinations of the singly occupied orbitals at the radical centers by their interactions with the σ and σ^* orbitals of the benzene ring is responsible for the singlet becoming the ground state of both **1a** and **1d** at angles around $\phi = 90°$.

As noted above, the lack of symmetry about $\phi = 90°$ of the singlet−triplet energy difference in **1d** must be due to the fact that the singly occupied MO of a nitroxyl group has a large coefficient on oxygen. The nitroxyl oxygens in **1d** interact with orbitals of the *m*-phenylene coupler in such a way that the maximum stabilization of the singlet, relative to the triplet, occurs around $\phi = 105°$ when the nitroxyls are *syn* to each other and around $\phi = 75°$ when they are *anti*. Presumably, at these geometries interactions between the oxygens and orbitals of the *m*-phenylene group increase the energy differences between the A and S NBMOs above the energy difference at 90°.

Due to the cylindrical symmetry of σ bonds, the interactions between the σ bonds of the *m*-phenylene group in **1d** and the nitroxyl orbitals are the same, whether the nitroxyl oxygens are on the same or the opposite side of the benzene ring. If the asymmetry about $\phi = 90°$ of the curves in Figure 1 were due to this type of interaction, the curves for *syn* and *anti* nitroxyls would, therefore, be the same. This is clearly not the case, since the stabilization of the singlet, relative to the triplet ($-2J$), reaches a maximum around $\phi = 105°$ when the nitroxyls are *syn*, but around $\phi = 75°$ when they are *anti*. Thus, the

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[16] Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

[17] The CASPT2N calculations were performed with the MOLCAS suite of *ab initio* programs: Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. MOLCAS, Version 2; University of Lund, Sweden, 1991.

[18] This was also the case when the size of the basis set was increased to 6-311+G (3df,2p). Thus, even with a very large basis set, through-space interaction between the nitroxyls in **1d** is calculated to make very little contribution to the singlet−triplet splitting.

[19] Reviews: Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369.

[20] These drawings of the NBMOs were made using the graphics package in Spartan, Version 3.1.2; Wavefunction, Inc.: Irvine, CA, 1994. The orbital plots for **1d** fail to show that the coefficients at the oxygens are considerably larger in magnitude than those at the nitrogens in the NBMOs.

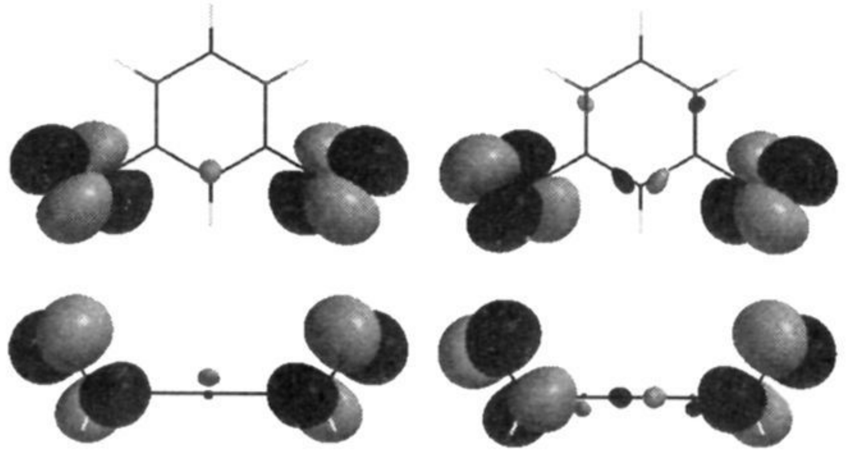

Figure 3. NBMOs at $\phi = 105°$ in *syn*-**1d**.[20]

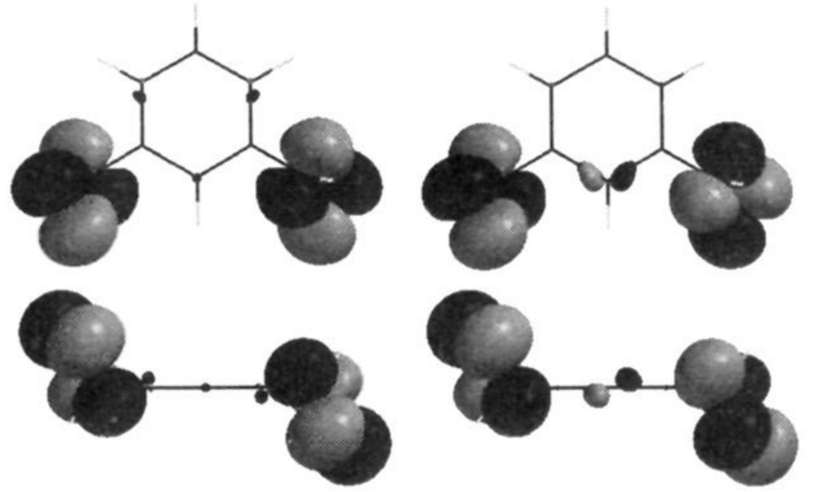

Figure 4. NBMOs at $\phi = 75°$ in *anti*-**1d**.[20]

asymmetry of the two curves in Figure 1 must be due to an interaction between the nitroxyl oxygens and the π and π^* orbitals of the benzene ring in **1d**.

As the nitroxyl groups rotate into conjugation with the benzene ring, the interactions between the A and S combinations of p$-\pi$ AOs on each nitrogen and the π and π^* MOs of the benzene ring give rise to NBMOs that resemble those of *m*-benzoquinodimethane.[14] To one of these NBMOs the ring contributes a p$-\pi$ AO at C-2. This AO is S with respect to a plane of symmetry that is perpendicular to the benzene ring, but A with respect to the 2-fold axis that lies in this plane. To the other NBMO the ring contributes the out-of-phase combination of p$-\pi$ AOs at C-4 and C-6, which has A symmetry with respect to this plane and S with respect to this axis. In both NBMOs the p$-\pi$ AOs of the ring are mixed with the p$-\pi$ AOs on the adjacent nitrogens in an out-of-phase fashion.

With which symmetry combination of singly-occupied nitroxyl orbitals the SA and AS p$-\pi$ AOs of the ring each mix obviously depends on whether there is a plane or axis of symmetry. When the nitroxyl groups are *syn*, only the plane of symmetry can exist; so the S combination of singly-occupied nitroxyl orbitals mixes with the SA p$-\pi$ AO at C-2, and the A combination of singly occupied nitroxyl orbitals mixes with the AS combination of p$-\pi$ AOs at C-2 and C-6. The resulting NBMOs for *syn* nitroxyls at $\phi = 105°$ in **1d** are depicted in Figure 3.

When the nitroxyl groups are *anti*, only the axis of symmetry can exist; so the S combination of singly-occupied nitroxyl orbitals mixes with the AS combination of p$-\pi$ AOs at C-2 and C-6, and the A combination of singly occupied nitroxyl orbitals mixes with the SA p$-\pi$ AO at C-2. The resulting NBMOs for *anti* nitroxyls at $\phi = 75°$ in **1d** are depicted in Figure 4.

For the *syn* nitroxyls at $\phi = 105°$ Figure 3 shows that in the S NBMO there is a bonding interaction between the AO at C-2 and the nitroxyl oxygens. The AO at C-2 can be seen to be hybridized toward the oxygens, which, of course, maximizes this interaction. This interaction provides a small amount of stabilization for the S NBMO, which was found in its ROHF orbital energy on going from $\phi = 90°$ to 105°.

In contrast, in the A NBMO the interaction of the AOs at C-4 and C-6 with the nitroxyl oxygens is antibonding. However, the AOs at C-4 and C-6 are, as shown in Figure 3, hybridized away from the oxygens, which minimizes this interaction. Consequently, the ROHF orbital energy of the A NBMO was found to change very little on going from $\phi = 90°$ to 105°.

Nevertheless, because the S orbital is stabilized at $\phi = 105°$, relative to $\phi = 90°$, the energy gap between the S and A orbital is larger at $\phi = 105°$ than at $\phi = 90°$. The increase in the energy difference between the two NBMOs is responsible for the increase in the magnitude of the singlet$-$triplet splitting, $2J$, for the *syn* nitroxyl groups on going from $\phi = 90°$ to 105°.

At $\phi = 75°$ the phasing of the p$-\pi$ AOs of the ring are reversed from those shown in Figure 3, because of the difference in which lobe of the p$-\pi$ AO on each nitrogen overlaps each face of the benzene ring. Consequently, at $\phi = 75°$ the S NBMO is destabilized and the A NBMO is stabilized, relative to $\phi = 105°$, by the interactions of the p$-\pi$ AOs of the ring with the nitroxyl oxygens. Because the difference between the S and A ROHF orbital energies is, consequently, smaller at $\phi = 75°$ than at $\phi = 105°$, the magnitude of the singlet$-$triplet splitting for the *syn* nitroxyl groups is smaller at $\phi = 75°$ than at $\phi = 105°$.[21]

When the nitroxyl groups are *anti*, the C_2 axis of symmetry causes the S combination of singly-occupied nitroxyl orbitals to mix with the AS combination of p$-\pi$ AOs at C-4 and C-6 and the A combination of nitroxyl orbitals to mix with the SA p$-\pi$ AO at C-2. The resulting NBMOs at $\phi = 75°$ are shown in Figure 4.

It can be seen in Figure 4 that in the S NBMO at $\phi = 75°$ there is a bonding interaction between the p$-\pi$ AOs at C-4 and C-6 and the nitroxyl oxygens, which is enhanced by the hybridization of the ring AOs toward the oxygen. More important, however, than the stabilization of the S NBMO is the destabilization of the A NBMO by an antibonding interaction between the p$-\pi$ AO at C-2 and the nitroxyl oxygens. Mixing of the p$-\pi$ AO on C-2 with the p$-\sigma$ AO on the same carbon causes the resulting p orbital at this carbon to be rotated out of the plane of the benzene ring in such a way that the bonding between this AO and the nitroxyl oxygens is smaller at $\phi = 75°$ than at $\phi = 90°$. The consequent destabilization of the A NBMO on going from $\phi = 90°$ to 75° was seen in its ROHF orbital energy.

Because in *anti*-**1d** the A NBMO is destabilized at $\phi = 75°$, relative to $\phi = 90°$, the energy gap between the S and A NBMOs is larger at $\phi = 75°$ than at $\phi = 90°$. The increase in the energy difference between the two NBMOs is responsible for the increase in the magnitude of the singlet$-$triplet splitting for the *anti* nitroxyl groups on going from $\phi = 90°$ to 75°.

The change in the phasing of the C-2 p$-\pi$ AO on going from $\phi = 75°$ to 105° causes the A NBMO to be stabilized at $\phi = 105°$ by the interaction between this AO and the nitroxyl oxygens. Therefore, the energy gap between the S and A NBMOs decreases between $\phi = 75°$ and 105°. This decrease

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[21] A similar type of non-nearest-neighbor interaction of the π orbitals of two twisted 2-methylenecyclopentane-1,3-diyls with the π orbitals of a *m*-phenylene linker would also serve to counteract the effect of the interaction of the π orbitals of the twisted triplet diradicals with the σ bonds of the linker. A near cancellation of the effects of these two interactions would leave the S and A combinations of the NBMOs of the twisted diradicals effectively degenerate. Such a cancellation might explain the apparent absence of antiferromagnetic coupling between the two twisted 2-methylenecyclopentane-1,3-diyls in a *m*-phenylene-linked tetraradical, prepared by Silverman and Dougherty.[7b]

in the energy difference between the two NBMOs is responsible for the decrease in the magnitude of the singlet–triplet splitting for the *anti* nitroxyl groups on going from $\phi = 75°$ to $105°$.[21]

At the maxima in Figure 1 around $\phi \approx 105°$ for *syn* nitroxyls and $\phi \approx 75°$ for *anti*, the singlet lies about -0.05 kcal/mol (≈ -18 cm^{-1}) below the triplet. This is about one-third of the size of the singlet–triplet splitting, $2J$, found in frozen samples of **2**[9] and crystalline samples of **3**,[10] but about three times that found in a dilute sample of **3** in PVC.[10] It is possible that the molecules of **3** in crystalline samples adopt conformations with values of ϕ that correspond to greater singlet–triplet splittings than the values of ϕ for molecules of **3** in PVC.

However, the X-ray structure of **3** finds that the nitroxyl groups are *syn* with an average value of $\phi = 70°$; and this geometry does not correspond to the maximum in Figure 1 for *syn* nitroxyl groups, which occurs near $\phi = 105°$. In fact, at $\phi = 70°$ in *syn*-**1d** the triplet is computed to be lower than the singlet by $2J = 0.01$ kcal/mol. Since the X-ray structure of **3** indicates that long-range *inter*molecular interactions do not play an important role in creating the negative values of $2J$ found in the crystalline sample of **3**, the computational results for *syn*-**1d** appear to be at variance with the experimental results for crystalline **3**.

However, **3** contains π-electron donating methoxyl groups at C-4 and C-6. In the *syn* conformation of **3**, only the A NBMO has any amplitude at these two carbons. The A combination of methoxyl p–π AOs lies lower in energy than the A NBMO; hence these methoxyl AOs are mixed into the NBMO in an antibonding fashion. Consequently, the methoxyl groups in **3** should raise the energy of the A NBMO, relative to the S NBMO, thus increasing the energy difference between the two NBMOs. As a result, $2J$ at $\phi = 70°$ is likely to be more negative in *syn*-**3** than in *syn*-**1d**.

In order to verify that this is the case, GVB and ROHF calculations were performed on the 4,6-dihydroxy derivative of **1d**, with *syn* nitroxyl groups fixed at $\phi = 70°$. The hydroxyl groups were constrained to lie in the plane of the benzene ring. The singlet–triplet splitting was, in fact, found to decrease from $2J = 0.01$ kcal/mol in *syn*-**1d** at $\phi = 70°$, but only to $2J = 0.00$ kcal/mol in the 4,6-dihydroxy derivative with similarly oriented nitroxyl groups.[22]

These GVB-ROHF calculations thus confirm that hydroxyl substitutents at C-2 and C-4 do have the expected qualitative effect on the singlet–triplet splitting. However, these calculations fail to account quantitatively for the finding that a crystalline sample of *syn*-**3** with an average value of $\phi = 70°$ was found to have $2J = -51.3$ cm^{-1} $= -0.15$ kcal/mol.[10] As noted earlier, it is certainly possible that calculations at the GVB-ROHF level underestimate the stability of the singlet, relative to the triplet, thus giving values of $2J$ that are too positive.

Conclusions

Our *ab initio* calculations on **1a** and **1d** find that, on twisting the radical-bearing groups at C-1 and C-3 out of conjugation with the benzene ring, the ground state changes from triplet to singlet. The change in ground state is due to through-bond, rather than to through-space, interactions between the radical centers that are connected by the *m*-phenylene linker. In the case of **1d** both σ and π orbitals of the benzene ring contribute to the energy difference between the NBMOs, and this leads to the maximum singlet–triplet splitting in **1d** occurring at different values of ϕ in the *syn* and *anti* conformers.

The results of our calculations on the 4,6-dihydroxy derivative of **1d** show that, by increasing the energy difference between the S and A NBMOs, the methoxyl groups at C-4 and C-6 of **3** stabilize the singlet state of the *syn* conformer at $\phi = 70°$, thus making $2J$ more negative than in **1d** at this geometry. However, the size of the calculated stabilization of the singlet is inadequate to explain quantitatively the value of $2J$ measured in a crystalline sample of *syn*-**3** with an average value of $\phi = 70°$.[10]

Nevertheless, our calculations do confirm qualitatively the recent experimental results on **2**[9] and **3**,[10] which show that *m*-phenylene is not invariably a ferromagnetic coupler. Our calculations find that, when radical centers at C-1 and C-3 are twisted sufficiently far out of conjugation with the aromatic ring, *m*-phenylene can act to couple the electrons on these centers antiferromagnetically.

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Supporting Information Available: Optimized GVB and ROHF/6-31G* geometries and energies for **1a** at $\phi = 0°$ and $90°$, for **1d** at $\phi = 0°$, and for the 4,6-dihydroxy derivative of *syn*-**1d** at $\phi = 70°$ (4 pages). Ordering information is given on any masthead page. This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[22] Calculations on the 4,6-dihydroxy derivative of *syn*-**1d** at $\phi = 0°$ give a triplet ground state, but with $2J = 0.18$ kcal/mol. This singlet–triplet splitting is 0.10 kcal/mol smaller than that in **1d** at $\phi = 0°$.