

CALIBRATION OF A SEMI-EMPIRICAL PROCEDURE FOR PREDICTING THE GROUND-STATE SPIN MULTIPLICITIES OF OPEN-SHELL MOLECULES. APPLICATIONS TO NEW SYSTEMS

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A semi-empirical configuration interaction (CI) algorithm is presented for predicting the ground-state spin multiplicity of open-shell systems. The computed energy gaps $\Delta E(\text{LS-HS})$ of model systems, Y-phenyl-X-phenyl-Y, where Y is a nitrene or nitroxide radical and X is an exchange coupling unit, are critically compared with the available experimental data. The current method has attenuated the deficiencies of the earlier algorithm proposed by Lahti and Ichimura and the predictions are qualitatively clearer, facilitating the classification of high- and low-spin topologies for isomeric species. The relative effectiveness of different exchange couplers can be discerned semi-quantitatively, and several new exchange couplers are described. The reasons for the qualitative failure of the earlier algorithm are discussed.

INTRODUCTION

In the area of high-spin molecules, theory and experiment have complemented each other in providing the basic understanding of the mechanisms through which unpaired electrons are exchange coupled via through-space and through-bond interactions.¹ The early work of Mataga,² followed by formal hypotheses constructed by Ovchinnikov,³ Klein⁴ and others⁵ relating the π -topology of a molecule to its ground-state spin multiplicity, has since motivated the synthesis of molecules which have very large spin quantum numbers in their ground states,⁶ and the characterization of single crystals of stable organic radicals⁷ which were found to have ferromagnetic properties at sub-liquid helium temperatures. However, such progress is limited to a handful of examples, while much research is still focused on the building blocks which may ultimately lead to materials with strong magnetic properties at higher temperatures.

A convenient model system for studying the effects of connectivity on the ground state can be designated as Y-phenyl-X-phenyl-Y where Y is an organic radical spin source and X is an exchange coupling unit. Qualitative theories based on valence bond^{3,4} (VB) and molecular orbital theory⁸ have provided much insight into the nature of exchange coupling in such systems but will

only be briefly described since many good reviews of the subject are available.^{1,9} Parity-based models such as those of Ovchinnikov³ and Klein⁴ are easily applied to alternant systems such as those where the π atoms can be starred and unstarred such that no starred or unstarred atoms are adjacent. Then the ground-state spin multiplicity is simply half the difference between the number of atoms in each set, $S = (n^* - n^0)/2$. Another model for diradicals in particular (but recently extended to systems with several unpaired electrons^{8b}) distinguishes between high-spin (HS) and low-spin (LS) systems based on the extent of atomic overlap of the non-bonding molecular orbitals (NBMO).⁸ If the NBMOs have atoms in common then the exchange interaction will favour the HS state and the molecule is said to be non-disjoint, while the disjoint system does not have atoms in common and therefore will have nearly degenerate electronic states and may be LS. For the model systems described in this paper, the two qualitative theories generally produce the same prediction of the ground-state spin multiplicity, but sometimes give conflicting predictions, as will be mentioned briefly below.

As part of the overall effort to design molecular magnetic materials, semi-empirical configuration interaction (CI) calculations have proved useful in exploring the relationship between ground-state spin multiplicity and structure, and for comparing the effectiveness of various exchange couplers.^{10,11} Recently, a large body of experimental work has been published on dimeric

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systems intended to serve as models for larger oligomeric and ultimately polymeric materials. Comparing the experimentally determined ground states with previous semi-empirical predictions showed that the latter incorrectly favoured high-spin states of disjoint diradicals. These systems were experimentally found to favour low-spin ground states by a small energetic margin. Such qualitative errors were discouraging, especially since there are few ways to predict reliably the behaviour of novel systems which are not amenable to qualitative theoretical analysis (an alternative computational procedure which also yields semi-quantitative predictions of the ground state uses a method based on approximately projected spin-unrestricted *ab initio* wave functions¹²).

In this paper, the qualitative and quantitative predictions of the ground-state multiplicity made by a semi-empirical CI method are critically compared with the available experimental data, and predictions for novel systems are made. The success and applicability of the method are assessed in order to provide calibrated data against which future predictions can be compared. The questions which this paper attempts to address are whether the limitations of the method are due to effects secondary to connectivity such as rotation, inherent procedural or program restrictions, or the approximations upon which the semi-empirical method is based. A reliable method is presented which can be easily and inexpensively applied to different systems and produces results of sufficient qualitative accuracy to be useful in guiding and corroborating the results of experiment.

COMPUTATIONAL METHODOLOGY

The basic procedure used previously by Lahti and Ichimura¹⁰ was adhered to in this study. Nitrenes and nitroxides have been used extensively as radical sources to test and compare the efficacy of exchange coupling between different isomers, therefore, these radicals were similarly used in computations. For a given isomer or conformer, the geometry of the state of highest spin multiplicity with maximum Kekulé bondedness was optimized subject to a planar constraint. The latter approximation is somewhat artificial, since twisting about various bonds could be expected in some cases. Experiments on decidedly non-planar compounds have revealed that planarity is not a necessary condition for exchange coupling to take place,¹³ but this restriction is computationally convenient which allows for the effects of rotation to be tested separately. Computing the geometry of other spin manifolds, although necessary when more precise energy differences are required as in *ab initio* studies, was found to have only a minor effect on the state energy differences for most species both in the previous study and in trial cases in the present one.

The advantages of using an unrestricted

Hartree-Fock (UHF) versus a restricted open-shell Hartree-Fock (ROHF) wave function for optimizing the high-spin state of diradicals are well known.¹⁴ However, a comparison of the geometries of *m*-phenylene-substituted diradicals computed by semi-empirical UHF and ROHF procedures showed these two geometries to be nearly identical, contradicting the results of more sophisticated *ab initio* calculations.¹⁵ It is important to note that geometries obtained by ROHF or UHF methods give slightly different (but not qualitatively conflicting) values of ΔE ; as long as either method for geometry optimization is used for all molecules in a given study, the results may be meaningfully compared. However, because the UHF wave functions for many of these extensively π -conjugated molecules were often contaminated by states of higher multiplicity, all geometry optimizations were based on ROHF wave functions.

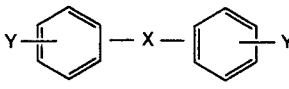






In experiments involving nitroxide free radicals, *tert*-butyl nitroxides are often employed. Previous *ab initio* calculations have found that the largest change of the spin density in the nitroxide moiety occurs when first one and then both of the hydrogens of the simplest nitroxide, ONH₂, are replaced by methyl groups.¹⁶ Further substitution by bulkier alkyl groups had only a mildly perturbing effect. Therefore, other than the difference in steric bulk, the substitution of a methyl for a *tert*-butyl group retains the primary electronic effects and hence seems to be a reasonable approximation. The AM1 hamiltonian was used extensively in the previous study^{17,18} (in Ref. 18, the qualitative results of a semi-empirical AM1/CI method are reported, using a similar algorithm). The PM3 hamiltonian,¹⁹ however, was slightly better at calculating nitroxide bonding parameters by comparison with experiment and so was used for all computations in this study.¹⁵ The state energy differences were calculated at the high-spin geometry for all states of interest [the OPEN(*N,N*) keyword was used where *N* = 4 and 2 for dinitrenes and dinitroxides, respectively, regardless of whether the system was predicted to be a closed singlet based on qualitative arguments; it should be mentioned that the AM1 hamiltonian tended to favour the high-spin state by a slightly larger amount than the PM3 hamiltonian in certain test cases]. A six-electron and five-orbital active space was used for small CI calculations for both dinitrenes and dinitroxides and represents only a minor change from the previous method which used a six-electron and six- or seven-orbital active space.

All semi-empirical calculations described in this paper used MOPAC version 6.01 as modified to run on the University of Tokyo's Hitachi M880 computer.²⁰

RESULTS AND DISCUSSION

In Table 1 are reported the computed low-spin to high-spin (LS-HS) energy gaps (ΔE) for model systems of

Table 1. Singlet–quintet and singlet–triplet energy differences (cal mol⁻¹) for phenylnitrenes and phenylnitroxides, respectively, Y, connected by various exchange coupling units X, with experimental values in parentheses

X	No.	Y			
			<i>p,p'</i>	<i>p,m'</i>	<i>m,m'</i>
	1a	N:		890 ^a	-0.2 (-242) ^b
	1b	Me–NO·	-910	590 ^c	-330 (-37) ^c
	2a	N:		700 ^d	1 (-69) ^d
	2b	Me–NO·	-833	630	-330
	3a	N:	800 ^e	6 (-110) ^e	3 (-76) ^e
	3b	Me–NO·	1150 (30) ^e	-116 (-10) ^e	100 (-5) ^e
	4a	N:	250	80	0 (-48) ^a
	4b	Me–NO·	360	50	10
	3c	N:	90	7	8
	3d	Me–NO·	12	-5	5
	4c	N:	38	10	5
	4d	Me–NO·	4	1	<1

^a Ref. 21.

^b Ref. 22.

^c Ref. 23.

^d Ref. 24, 25.

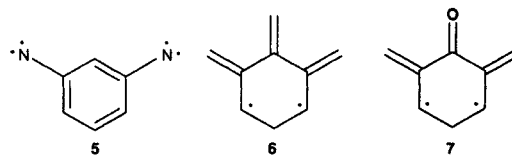
^e Ref. 26.

phenylnitrenes and phenylnitroxides connected by various π -conjugated exchange couplers. Experimental values are reported where such data are available. It is stated at the outset that the numbers reported in Table 1 are smaller than one would ordinarily consider definitive in the *ab initio* sense without the use of large basis sets and extensive electron correlation. The method was judged by the ability to reproduce and predict experimental results and not by comparison with higher levels of theory.

Dinitrenes

The series of dinitrene isomers **1a**, **2a**, **3a** and **4a** show a number of interesting trends. When an HS ground state is predicted for a given isomer by VB theory and can also be considered non-disjoint, that is, compounds **1a-p,m'**, **2a-p,m'**, **3a-p,p'** and **4a-p,p'**, the ground state is computed to be a quintet, in agreement with experiment. The magnitude of this preference for the planarized compounds is predicted to be rather small, usually less than 1 kcal mol⁻¹ (1 kcal = 4.184 kJ). The previous AM1/CI method using a CI matrix of the same dimension, but selecting a subset of the configurations generated from a slightly larger active space, predicted ΔE (singlet–quintet) of 4.0, 2.7, 8.5, and 0.4 kcal mol⁻¹ for **1a-p,m'**, **2a-p,m'**, **3a-p,p'** and **4a-p,p'**,

respectively.¹⁰ While the qualitative results are the same as in this work, these values are considerably larger than those reported in Table 1, and the size of ΔE was different for these topologically related species. Unfortunately, it is not possible to compare computed and experimental energy differences for these HS isomers because of difficulties in obtaining these values experimentally. For this set of molecules in particular, the experimental evidence indicates that the quintet ground state lies below the excited triplet and singlet states by an energetic margin that prevents significant thermal population of the excited states at the temperatures used for these experiments. Because experiment can only estimate a lower limit above which ΔE is likely to lie, it is not possible to choose a computed value which best represents the actual absolute energy difference. For comparison, *m*-phenylenedinitrene (**5**) (Scheme 1)



Scheme 1

was predicted by the current method to have a ΔE_{SQ} of $13.9 \text{ kcal mol}^{-1}$ [ab initio value at the ROHF geometry is $10.7 \text{ kcal mol}^{-1}$ (Ref. 27)]. The exchange coupling in **1a-p,m'** may be three times [$4.0 \text{ kcal mol}^{-1}$ (Ref. 10)] less effective than **5** or may be more than an order of magnitude weaker (*ca* $0.9 \text{ kcal mol}^{-1}$). The latter prediction is not unreasonable considering the separation between radical centres, but these values are only an estimate which future experimental and theoretical work must verify.

Computationally, the *m,m'*-isomers of dinitrenes **1a**, **2a**, **3a** and **4a**, and the *p,m'* isomers of **3a** and **4a** are all predicted to have very small singlet–quintet energy gaps. Taken literally, these values would suggest that **4a-m,m'** has a small preference ($\Delta E_{\text{SQ}} = 81 \text{ cal mol}^{-1}$) for a quintet ground state, whereas the other molecules have nearly degenerate singlet, triplet and quintet states ($-0.2 < \Delta E_{\text{SQ}} < 6 \text{ cal mol}^{-1}$). These compounds were all found to be ground-state singlets experimentally, in qualitative disagreement with most of the computed results. It is apparent that this method is not sensitive enough to distinguish between different degrees of anti-ferromagnetic coupling for these dinitrenes. However, the magnitude of the calculated ΔE_{SQ} is clearly much smaller for these disjoint connectivities than for the non-disjoint cases, and hence serves to distinguish between π -topologies which are ferromagnetically coupled and those which are nearly degenerate or anti-ferromagnetically exchange coupled. For comparison, $\Delta E(\text{singlet–quintet})$ for **1a-m,m'**, **2a-m,m'**, **3a-p,m'**, **3a-m,m'**, **4a-p,m'** and **4a-m,m'** computed by the previous method were 0.8, 1.2, 2.4, 2.7, 0.7, $0.5 \text{ kcal mol}^{-1}$, respectively.¹¹ A quintet ground state was predicted by a relatively large margin by the earlier method, contrasting with the results listed in Table 1, which are qualitatively closer to experiment and predictions made by Borden and Davidson's^{8a} disjoint model. Nevertheless, the preference of the HS state for dinitrenes still seems to be overestimated by the current method for connectivities which are formally considered to be disjoint.

Dinitroxides

The computational results for the dinitroxides **1b**, **2b**, **3b**, and **4b** generally follow the trends observed for the various dinitrene isomers. The qualitative predictions for the through-bond couplers vinylene and ethynylene were found to agree with experiment, but quantitatively the computed magnitude of ΔE_{ST} for the *m,m'*-isomers of **1b** and **2b** was found to be larger than experiment. The exact reason for the overestimation of ΔE_{ST} may be partially accounted for by twisting about one or both of the phenyl and nitroxide groups, as will be discussed in more detail below. No experimental values of ΔE_{ST} are available for **1b-p,p'** and **2b-p,p'**, but the large anti-ferromagnetic coupling most likely results from the

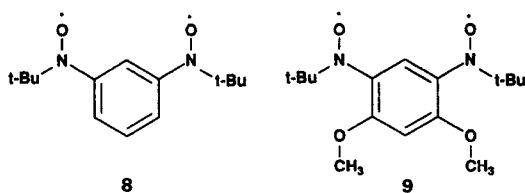
energetic stabilization by closed shell Kekulé resonance structures similar to those found for **1a** and **2a-p,p'** dinitrene (see below). Hence, if the closed shell singlet form of these molecules were optimized, ΔE_{ST} would probably be fairly large. There are several closed-shell configurations in the singlet CI wave functions of **1b-p,p'** and **2b-p,p'** which are important energetically, supporting this notion. By contrast, the singlet CI wave functions for other dinitroxides which could not form Kekulé structures were dominated primarily by open-shell configurations, as would be expected for two localized nitroxide radicals.

The computed ΔE_{ST} for dinitroxides exchange coupled through the cross-conjugated vinylidene spacer do not strictly follow the experimental trends. PM3/CI calculations overestimate the stability of the triplet and singlet states of **3b-p,p'** and **3b-p,m'** respectively, while predicting that **3b-m,m'** should be a ground-state triplet by about 99 cal mol^{-1} . Experiment contradicts the latter predictions, finding ΔE_{ST} to be small and negative at $-5.2 \text{ cal mol}^{-1}$.²⁷ Geometric torsion reduces ΔE_{ST} , bringing some of the computed results closer to experiment. However, *ab initio* CI calculations²⁸ using polarized basis sets found a triplet ground state for connectivity related pentamethylenepropane derivatives, **6** and **7** (Scheme 1), so future experiments must decide whether a planarized version of **3a-m,m'**, **3b-m,m'** and **4a-m,m'** remain low-spin.²¹

The carbonyl spacer is π -isoelectronic with vinylidene and was predicted at the *ab initio* level of theory to be a weaker exchange coupler.²⁹ The first experimental support of this prediction is evidenced by comparison of dinitrenes **4a-m,m'** and **3a-m,m'**, where $\Delta E_{\text{SQ}} = -48$ and -76 cal mol^{-1} , respectively (the qualitative models described in the Introduction yield conflicting predictions for the ground state spin of the isomers of **3** and **4**; for detailed theoretical and experimental discussions on the carbonyl and vinylidene spacers, see Refs 21 and 26). While the carbonyl spacer appears to be weaker at the semi-empirical level for dinitroxides **3b-p,p'** and **4b-p,p'** and dinitrenes **3a-p,p'** and **4a-p,p'**, the predictions vary from this pattern especially for the *p,m'*-isomers. Possible reasons for this discrepancy are described below, but the important distinction between topologies of different exchange coupling ability can still be made. Although no experimental data are available for compounds **4b**, it is likely that the exchange coupling through this spacer is slightly weaker than the 1,1-ethenediyl-linked nitroxides. This would make experimental determination of the energy differences difficult since ΔE_{ST} for **3b** are already very small.

Computationally, dinitroxides are predicted to have nearly the same energy differences as the dinitrenes. However, the experimental results in Table 1 show that the dinitroxides are much more weakly exchange coupled than the comparable dinitrene derivatives. The

smaller magnitude of the experimental ΔE_{ST} of dinitroxides compared with dinitrenes most likely reflects the inherently weaker ability of a localized nitroxide radical to polarize neighbouring electron spins. This must be in part due to the sterically bulky *tert*-butyl groups which cause torsion about the nitroxide–phenyl bond, thereby decreasing the overlap of the p-orbital of the nitrogen atom with the π -system. X-ray crystal structures of single crystals of a variety of phenylnitroxides have shown that the *tert*-butylnitroxide groups are rotated out of the plane of the phenyl ring anywhere from 29 to 37° when no substituent *ortho* to the nitroxide group is present, while the dihedral angle is much larger for *ortho*-substituted nitroxides.^{30,31} At cryogenic temperatures in rigid media typically used during experimental studies, it is likely that the *tert*-butylnitroxide groups also adopt such a conformation. As a result, the phenol π -electrons are polarized to a lesser extent, thus reducing the effectiveness of the through-bond interaction leading to smaller singlet–triplet gaps. This effect has been observed experimentally in compounds **8** and **9** (Scheme 2), where the former is a ground-state triplet experimentally but the larger torsional angle of the latter actually results in a ground-state singlet.³¹



Scheme 2

Geometry optimization of species **1b**, **2b**, **3b** and **4b** results in a planar nitroxide group which lies in the plane of the carbon framework. Hence, the overestimation of the computed ΔE_{ST} may be due in part to the favourable overlap which the planar conformation provides. When the effect of twisting of the nitroxide and phenyl groups is taken into account computationally, ΔE_{ST} was found to decrease in a regular fashion as the twist angle became larger. For example, the effect of twisting one phenyl ring of the cross conjugated species by 90° is presented in Table 1 as species **3c**, **3d**, **4c** and **4d**. The energy differences are greatly reduced and, in the case of the dinitroxides, the ΔE_{ST} are in much better agreement with experiment. As a further example, when both the phenyl and nitroxide groups of **1b** were arbitrarily twisted by 60° and 20°, respectively, ΔE_{ST} was -360 , 340 and -60 cal mol⁻¹ for the **1b**-*p,p'*, **1b**-*p,m'*, and **1b**-*m,m'* isomers, respectively. The last value compares favourably with experiment [$\Delta E_{ST} = -37$ cal mol⁻¹ (Ref. 23)] for **1b**-*m,m'*. However, torsion about one or both of the phenyl rings does

not change the prediction of nearly degenerate states for the disjoint dinitrenes **1a**-*m,m'* and **2a**-*m,m'*, while ΔE_{SQ} decreases in a regular fashion to very small but positive values of ΔE_{SQ} for the non-disjoint dinitrenes **1a**-*p,m'* and **2a**-*p,m'*. Therefore, while rotation at the computational level generally reduces ΔE_{ST} , increasing the agreement with experiment in the dinitroxide cases, not all of the discrepancies between theory and experiment in Table 1 are removed by this explanation.


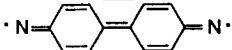
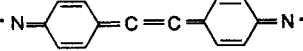
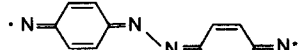
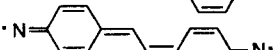
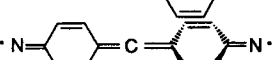
If the magnitudes of the computed ΔE_{ST} for the non-disjoint dinitrenes are used to order the efficiency of through-bond exchange coupling, the order would be from most effective to least effective: vinylene > vinylidene > ethynylene > carbonyl. This differs from the experimental ordering obtained from the results on disjoint dinitrenes: vinylene > ethynylene > vinylidene > carbonyl. Further, the π -topology of **3a** and **4a**-*p,m'* couples the unpaired electrons more effectively than compounds **3a** and **4a**-*m,m'*, in agreement with the qualitative argument that the latter are 'doubly disjointed'.²⁶ As mentioned above, the semi-empirical method is not able to distinguish correctly between these topologies. However, the computational results for the HS non-disjoint dinitrenes roughly corresponds to the experimental ordering.

Localized dinitrenes

The energy differences between the singlet and triplet states of the *p,p'*-isomers of the dinitrene series of compounds are presented separately in Table 2 because they are different electronically from the other non-Kekulé dinitrenes as evidenced by their EPR spectra.³² Although these compounds are not new from an experimental standpoint, they are interesting because the compounds that have been studied exhibit triplet EPR signals with zero-field splitting parameters that do not scale with the distance between radical centres.³³ That is, if the interelectron distance is taken to be the distance between nitrogen atoms, then the *D* value would be predicted to be considerably smaller than what was observed. From parity-based arguments, these compounds should all be ground-state singlets, but it was only recently that the first experimental value was reported for *p,p'*-biphenyldinitrene.³³ The quinoidal form of *p*-phenylenedinitrene was confirmed by IR experiments³⁴ and supported by vibrational analysis at the *ab initio* level using a polarized basis set.²⁷ *Ab initio* CI calculations showed the singlet–triplet energy separation to be very small (60 cal mol⁻¹) with the two unpaired electrons essentially localized to nitrogen p-orbitals.

The series of diradicals in Table 2 have decreasing ΔE_{ST} as the distance between radicals increases and are all predicted to be ground-state singlets (**13** excluded). Recent experimental data on compounds **10**, **11** and **12** support these qualitative predictions.³⁵ While the result

Table 2. Energy differences between the singlet and triplet states of a series of localized dinitrenes

Formula	No.	ΔE_{ST} (cal mol ⁻¹)
	10	-390
	11	-120 (-583) ^a
	2a- <i>p,p'</i>	-90
	12	-50
	1a- <i>p,p'</i>	-34
	13	7

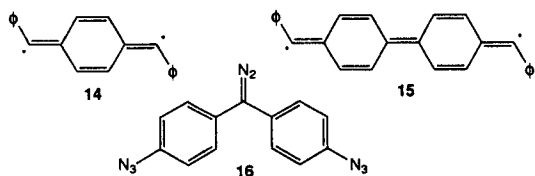
^a Ref. 34.

for species **10** contradicts *ab initio* results and no literature value exists for this compound, the related diphenyldicarbene **14** (Scheme 3) was found to have a singlet GS by *ca* 590 (Ref. 36) to 850 cal mol⁻¹ (Ref. 37), and it is likely that ΔE_{ST} for **10** is similar in magnitude to the predicted value of -388 cal mol⁻¹. *p,p'*-Biphenyldinitrene was computed to be a ground-state singlet by -115 cal mol⁻¹. While this value is qualitatively correct, **11** was found experimentally to favour the singlet state by -583 ± 120 cal mol⁻¹, an energetic margin larger than predicted.³³ An experimental study on the analogous *p,p'*-biphenyldiphenylcarbene system **15** (Scheme 3) found that the observed triplet state was energetically above the singlet ground state.³⁸ *p,p'*-Stilbenedinitrene, **1a-p,p'**, was also reported to be a ground-state singlet experimentally,³⁵ although computationally, the small preference for a singlet state by -34 cal mol⁻¹ may be underestimated by comparison with the data for **10** and **11**. Nevertheless, singlet coupling may be expected for species **2a-p,p'** and **12**³⁹

because of the similar electronic nature of these species and the trends displayed in Table 2. Species **13** in Table 2, which may be formed after photolysis of **16**, is predicted to have a triplet GS by a very small amount, 7 cal mol⁻¹. Although this compound was constrained to have *D*_{2d} symmetry during optimization, the small preference for a triplet GS may result more from an HS connectivity than from the symmetry-enforced degeneracy of the non-bonding molecular orbitals. The ground state and the mechanism by which the unpaired electrons are exchange coupled in **13** must be determined by experiment. Overall, the agreement between theory and experiment seems fairly good for these molecules, considering that the triplet state was optimized and used in calculations of the energy differences while these species were generally found to be ground-state singlets.

2,6-Dimethylenanthracenediyl-3,6-dioxy (**17**) and 3,6-dimethylenanthracenediyl-1,7-dioxy (**18**)

As a final test of the semi-empirical procedure, it was decided to predict the GS spin multiplicity of **17** (Figure 1), since this species was found to be a triplet ground state experimentally⁴⁰ but is predicted by valence bond arguments to be a GS singlet. Just for comparison purposes, the geometry was optimized for each state separately. The differences in the singlet and triplet geometries were minimal, but the quintet geometry was no longer quinoidal in form and had longer O—C bond



Scheme 3

	Electronic State		
	Q	T	S
Q	11.9	0.54	0
Geometry T	22.9	0	0.03
S	19.1	0.07	0

Figure 1. Comparison of geometry and LS-HS energy differences in kcal mol⁻¹ for diradical 17. All energy differences are relative to the state of lowest energy at each geometry

lengths. At the triplet geometry the triplet state was predicted to be the ground state by a small energetic margin, 30 cal mol⁻¹, in agreement with experiment. At both the quintet and singlet geometries, however, the singlet was predicted to be the ground state by 540 and 70 cal mol⁻¹, respectively, in agreement with parity-based arguments. It is encouraging that the semi-empirical method made the correct prediction of the GS at the triplet geometry, since if only one state were to be optimized, as is suggested in this paper, it would be the triplet state with maximum Kekulé bondedness. The quintet state of 17 was predicted to lie above the singlet and triplet states by a large energetic margin, while 18 (Figure 1) was predicted to be a GS quintet by an almost equally large gap of 8.0 kcal mol⁻¹, in qualitative agreement with experiment.⁴¹ These results are encouraging but should be taken as estimates of ΔE and not literal quantitative values. Rather, the data suggest that the triplet and singlet states of 17 are very close in energy while the quintet state can be considered to be a high-lying excited state.

Procedure and program limitations

While the general experimental trends within a series of isomers for both dinitrenes and dinitroxides are qualitatively reproduced by the present method, torsion alone cannot be wholly responsible for the overestimation of ΔE in certain cases, and the discrepancies among isoelectronic or connectivity-related molecules in others. Perhaps the best way to improve the fit to the experimental data would be to use a larger active space in performing the CI. However, because of the present program limitations inherent to MOPAC, choosing a larger active space does not improve the qualitative

accuracy. In the previous work, a six-electron, in six-orbital (6,6) active space was typically used for computing all state energies. For diradical species, this included two closed-shell orbitals, two half-occupied and two virtual orbitals in the CI, whereas for dinitrenes, one doubly occupied, four half-filled and one virtual orbital were used. This generated a total of 400, 225 and 36 configurations for the singlet, triplet and quintet (for dinitrenes) states, respectively. Unfortunately, the CI in MOPAC is limited to a matrix of dimension 100 and therefore only a subset of the configurations are kept. Since more singlet configurations are generated than quintet or triplet configurations for an active space of a given size, truncating the number of configurations to 100 results in an unequal treatment of each state by MOPAC. In fact, the resulting electronic states were not always pure spin states, as evidenced by the non-integer expectation values of the S^2 operator, suggesting that some crucial configurations had been omitted. Therefore, the previous algorithm using the larger (6,6) active space had a tendency to overestimate the stability of the high-spin states.

The present study employed a (6,5) active space, which generates 100, 50 and 5 configurations for the singlet, triplet and quintet states, respectively, which is sufficient to provide a proper description of each electronic state for both dinitrenes and dinitroxides. However, dinitrenes no longer have a π -antibonding MO to accept excitations in the CI whereas dinitroxides do. This may result in the qualitative inaccuracy observed for the disjoint dinitrenes and lead to energy gaps which are underestimated for non-disjoint dinitrenes, since it was noted that smaller active spaces often led to smaller energy differences in a number of test cases. However, there is usually a large enough difference in ΔE_{SQ} between topologies that are HS and those that are LS to allow distinction between them. Therefore, despite the smaller number of configurations, the qualitative predictions are arguably clearer and closer to experiment with the smaller (6,5) active space. An upper limit for the number of open shells is thus limited to four and possibly five, if qualitatively correct results are desired.

In addition, the similarity of UHF and ROHF geometries at the semi-empirical level suggests fundamental problems which may be more difficult to overcome.¹⁵ It was noted, for example, that nitrene and carbene bond lengths were considerably shortened by comparison with high-level *ab initio* calculations, and were almost identical for both UHF and ROHF wavefunctions. While geometries may be improved by a set of parameters specific for these hypovalent species, the change in the qualitative predictions of the ground state are not likely to differ significantly. The modified neglect of diatomic differential overlap approximation on which the semi-empirical program is based systematically neglects all three- and four-centred inter-

grals.⁴² This approximation may be more severe for open-shell diradical systems which often exhibit long-range intramolecular spin-spin coupling, but it is difficult to pinpoint specific effects which directly pertain to ΔE . While it is clear from Tables 1 and 2 that the semi-empirical CI method is fairly successful in qualitatively distinguishing between LS and HS topologies in most of the above examples, particularly after the identification of the best active space for the CI, caution is advised when making specific quantitative predictions about the magnitude of the energy differences for individual molecules.

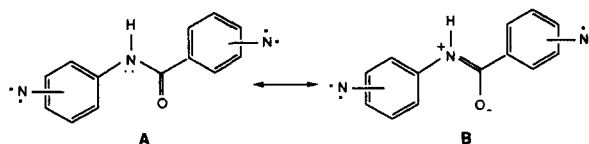
Having thus identified problem areas and defined the range of applicability, the discussion will now turn to a few novel exchange couplers which may prove to be useful in the design of high-spin molecules. The results for these new systems are presented in Table 3.

Amide bond

The amide bond is a synthetically attractive spacer which has the potential to form hydrogen bonds with adjacent molecules and also one-dimensional polypeptide chains. If the amide bond was able to couple unpaired electrons effectively, its introduction into an oligomer or polymer may eventually help realize not only one-dimensional spin alignment but also the intermolecular interactions necessary for bulk magnetism by

providing a cohesive force through hydrogen bonds. Other functional groups pendant to a phenyl ring with hydrogen bonding potential could also be used for this purpose. However, as a first step, the effectiveness of the amide bond as an exchange coupler will be evaluated by the current procedure.

It is typical to think of the amide bond as existing in two resonance forms, both of which may conceivably operate to intramolecularly couple distant unpaired electrons. Resonance structure **A** (Scheme 4) might be



Scheme 4

thought of as a three π -electron coupler where the lone pair on the nitrogen would act as a superexchange centre, and thus qualitatively, the p,p' - and m,m' -isomers would be expected to be high-spin whereas the p,m' - and m,p' -isomers would be low spin. On the other hand, resonance structure **B** is obviously similar to vinylene and therefore the regioselectivity should be identical with that for the stilbene derivatives **1**. The

Table 3. Singlet–quintet and singlet–triplet energy differences (cal mol⁻¹) for phenylnitrenes, and phenylnitroxides, Y, connected by various exchange coupling units, X, with experimental values in parentheses

X	No.	Y				
			p,p'	p,m'	m,p'	m,m'
	19a	N:	-170 (< -180) ^a	169	70	3 (-39) ^a
	19b	Me-NO [•]	-7	74	70	-30
	19c	CH ₂	-270	200	150	-90
	20a	N:	-320 (-300) ^b	70 (>0) ^b		<1 (-1.2 < ΔE < 0) ^b
	20b	Me-NO [•]	-50	0		-20
	21a	N:		290		0
	21b	Me-NO [•]	-910	590		-390
	22	N:	1440	150		2
	23	N:	-5400	2340		140

^a Ref. 43.

^b Ref. 44.

energy differences for **19a** in Table 3 indicate that the latter mechanism may be operative. In the case of the amide bond, the qualitative results are clear in that the p,m' - and m,p' -isomers are predicted to have high-spin ground states, the p,p' -isomer is a ground-state singlet, and the m,m' -isomer has nearly degenerate triplet and singlet states or may be low spin. The dinitroxide (**19b**) and dibenzyl (**19c**) species follow the identical trend except for the m,m' case, which was predicted to be low spin coupled by a small amount. Species **19c** is π -isoelectronic with **19a** so that it is not so surprising that the magnitude of ΔE_{SQ} is nearly the same for these compounds. The magnitude of the preference for the HS state is predicted to be less than the fully π -conjugated species **1–4**, but the difference is large enough so that oligomeric and polymeric systems may still remain high spin. The amide bond is therefore regarded as being worthy of experimental investigation in order to confirm its effectiveness as an exchange coupler.⁴³

Disilanes

Disilanes [Y-Si(CH₃)₂Si(CH₃)₂-Y] (**20**), where Y is a phenyl group carrying a nitrene or nitroxide substituent, are of interest as novel exchange couplers because the possibility for σ - π interaction exists with the proper conformation. While full computational and experimental details on the dinitrene-substituted compounds are reported together in a separate publication,⁴⁴ the inclusion in this paper of the principal results seems justified to show the diverse systems to which the semi-empirical method is applicable. The p,p' -isomer was computationally found to be a ground-state singlet by $-323 \text{ cal mol}^{-1}$ for the dinitrene case, in very good agreement with experiment ($-300 \text{ cal mol}^{-1}$). The closeness of the results in this case must be considered fortuitous based on the above discussion, but it is nevertheless an encouraging result. The data for the p,m' - and m,m' -isomers also compare favourably with experiment, suggesting that the observed ground-state spin multiplicities of the disilanes may be qualitatively explained by a parity-based model. The ground state was influenced by conformation at the computational level,⁴⁴ however, and as the σ - π overlap decreased with rotation, so did the efficiency of exchange coupling. The p,p' - and m,m' -isomers of the dinitroxides **20b** are weakly antiferromagnetically coupled by -50 and -20 cal mol^{-1} , respectively, while the p,m' -isomer was predicted to have degenerate triplet and singlet states. The energy differences are smaller than for **20a**, as would be expected for a nitroxide as the radical source, but the disilane spacer appears to be much weaker than the π -conjugated spacers or even the amide bond for coupling unpaired electron spin.

Azobis(arylnitrene)

Species **21** is π -isoelectronic with *trans*-stilbene and, unsurprisingly, has ΔE values which are very similar to those for **1a** and **1b**. The largest difference is in the prediction for **21a-p,m'**, the non-disjoint dinitrene isomer, where ΔE is approximately one third of the value for **1a-p,m'**. This is not a serious deficiency, and was mostly likely due to the replacement of a π -bonding orbital by a nitrogen lone-pair orbital in the CI. This did not occur for the m,m' -isomer and was case specific. The best remedy would be to increase the dimension of the CI matrix so that more orbitals could be included, thus decreasing the importance of a slight mixing of π -bonding and non-bonding MOs.

Dicyano-vinylidene and protonated carbonyl

It is interesting to consider whether chemical modification of a basic coupling unit could lead to different ground-state properties. The dicyano (**22**) and protonated carbonyl (**23**) groups are examples of such alterations which act in a similar manner by withdrawing charge from the double bond. For **22**, the ground-state predictions closely follow those for the unsubstituted vinylidene group. The ΔE_{SQ} energy difference for **22-p,p'** was predicted to be twice as large as that for **3a-p,p'**, while the m,m' -isomer remains disjoint and the p,m' -isomer is predicted to have a quintet ground state by a smaller amount compared with the p,p' -isomer. Inspection of the ethene C=C bond length shows that it is longer than the unsubstituted species and the phenyl-ethene bonds are correspondingly shorter. This suggests that having electron-withdrawing groups at one terminus weakens the central bond and permits greater delocalization through the vinylidene spacer, thus increasing the exchange coupling efficiency. This effect should manifest itself for the other two isomers in making them more strongly singlet coupled, contrasting with the results in Table 3. Based on the theoretical and experimental data for **3a**, it is likely that the results for **22-p,m'** and **22-m,m'** are qualitatively incorrect and would be found to be GS singlets experimentally. However, the vinylidene spacer has proved troublesome for the semi-empirical method¹¹ and so the results in Table 3 can still be interpreted to imply that the p,p' -isomer will have an HS ground state and the p,m' - and m,m' -isomers will be LS or have nearly degenerate electronic states, respectively.

The situation is remarkably different for **23**, which suddenly behaves like a biphenyl-type connectivity.³⁴ The proton withdraws more charge from the carbonyl bond than the dicyano substituents did from vinylidene at the computational level, leaving the carbonyl carbon atom with a large positive charge. The absence of a

π -electron at this atom implies that this atom should be skipped when applying a parity-type rule to this system, so that the p,p' -connectivity becomes LS, the p,m' -isomer becomes HS, and the m,m' -isomer continues to behave as if it had nearly degenerate states by comparison with the other much larger values of ΔE_{SQ} . However, this calculation was somewhat artificial since the total charge was not balanced as it would be in solution or under matrix conditions, and this may cause a spurious change in the computed geometry and thus the ground-state predictions. Nevertheless, the possibility for enhancing or changing the nature of certain exchange couplers by appropriate substituents or doping remains an interesting area for future experimental research.

CONCLUSIONS

A minor modification of the previous semi-empirical CI procedure has removed the ambiguity in the prediction of the ground-state spin multiplicity for dimeric model systems. Topological differences between isomers are generally clearer and the computed values for the high-spin species allow for a semi-quantitative ordering of the various exchange couplers from most to least effective which differs only slightly from experiment. In favourable cases, the computed energy gap comes reasonably close to the measured value of ΔE . Geometric torsion was found to decrease the energy gaps in a regular manner for most of the diradicals studied, and brought the computed ΔE_{ST} more in line with experiment for the dinitroxides in particular. Specific problems still occur, particularly for disjoint dinitrenes predicted to be HS by a small amount, but which have been found to be LS experimentally. Torsion has little effect on these molecules and modification of the program to increase the size of the CI matrix may be necessary before qualitative accuracy is achieved for these species. The extent to which the NDO approximation affects the predictions, in terms of both the computed geometries and the size and sign of ΔE , is still not well understood. The method is expected to be most useful for compounds where the ground state is not easily predicted by simple theoretical models.

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REFERENCES

- D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio (Eds.), *Magnetic Molecular Materials*, Vol. 198E. Kluwer, Dordrecht (1991).
- N. Mataga, *Theor. Chim. Acta.* **10**, 273 (1968).
- A. A. Ovchinnikov, *Theor. Chim. Acta* **47**, 297 (1978).
- D. J. Klein, *Pure Appl. Chem.* **55**, 229 (1983); D. J. Klein and S. A. Alexander, in *Graph Theory and Topology in Chemistry*, edited by R. B. King and D. H. Rouvray, Vol. 51, p. 404. Elsevier, Amsterdam.
- M. Shen and O. Sinanoglu, in *Graph Theory and Topology in Chemistry*, edited by R. B. King and D. H. Rouvray, Vol. 51, pp. 373–403. Elsevier, Amsterdam (1987).
- N. Nakamura, K. Inoue, H. Iwamura, T. Fujioka and Y. Sawaki, *J. Am. Chem. Soc.* **114**, 1484 (1992).
- M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett.* **186**, 401 (1991); K. Inoue and H. Iwamura, *Adv. Mater.* **4**, 801 (1992); R. Chiarelli, A. Rassat and P. Rey, *J. Chem. Soc., Chem. Commun.* 1081 (1992).
- (a) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.* **99**, 4587 (1977); (b) J. Pranata, *J. Am. Chem. Soc.* **114**, 10537 (1992).
- H. Iwamura, *Adv. Phys. Org. Chem.* **26**, 179 (1990).
- P. M. Lahti and A. S. Ichimura, *J. Org. Chem.* **56**, 3030 (1991).
- P. M. Lahti and A. S. Ichimura, *Mol. Cryst. Liq. Cryst.* **176**, 125 (1989).
- K. Yamaguchi, M. Okumura and T. Noro, *Chem. Phys. Lett.* **190**, 353 (1992); M. Okamura, K. Takada, J. Maki, T. Noro, W. Mori and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.* **233**, 33 (1993), and references cited therein.
- J. Veciana, C. Rovira, M. I. Crespo, O. Armet, W. M. Domingo and F. Palacio, *J. Am. Chem. Soc.* **113**, 2552 (1991).
- W. T. Borden, E. R. Davidson and D. Feller, *Tetrahedron* **18**, 737 (1982); W. T. Borden, in *Diradicals*, edited by W. T. Borden, p. 23., Wiley, New York (1982).
- A. S. Ichimura and H. Iwamura, unpublished results.
- B. Gillon, P. Becker and Y. Ellinger, *Mol. Phys.* **48**, 763 (1983).
- M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
- T. P. Radhakrishnan, *Chem. Phys. Lett.* **181**, 455 (1991).
- J. J. P. Stewart, *J. Comput. Chem.* **10**, 209 (1989).
- J. J. P. Stewart, *MOPAC Version 6*, QCPE No. 455; revised as Version 6.01 by T. Hirano, Ochanomizu Women's University (1992).
- C. Ling, M. Minato, P. M. Lahti and H. van Willigan, *J. Am. Chem. Soc.* **114**, 9959 (1992).
- T. Doi, Master's Thesis, University of Tokyo (1993).
- T. Watanabe, N. Koga and H. Iwamura, unpublished results.
- H. Iwamura and S. Murata, *Mol. Cryst. Liq. Cryst.* **176**, 33 (1989).
- S. Murata and H. Iwamura, *J. Am. Chem. Soc.* **113**, 5547 (1991).
- T. Matsumoto, T. Ishida, N. Koga and H. Iwamura, *J. Am. Chem. Soc.* **114**, 9952 (1992).
- A. S. Ichimura and P. M. Lahti, *Mol. Cryst. Liq. Cryst.* **233**, 33 (1993).
- A. S. Ichimura, PhD Dissertation, University of Massachusetts, Amherst, MA (1992).
- A. S. Ichimura, A. R. Matlin and P. M. Lahti, *J. Am. Chem. Soc.* **112**, 2868 (1990); M. B. Coolidge, K. Yamashita, K. Morokuma and W. T. Borden, *J. Am.*

- Chem. Soc.* **112**, 1751 (1990); W. T. Borden, *Mol. Cryst. Liq. Cryst.* **232**, 195 (1993).
30. F. Kanno, K. Inoue, N. Koga and H. Iwamura, *J. Phys. Chem.* **97**, 13267 (1993).
31. F. Kanno, K. Inoue, N. Koga and H. Iwamura, *J. Am. Chem. Soc.* **115**, 847 (1993).
32. E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo and G. Smolinsky, *J. Am. Chem. Soc.* **88**, 5076 (1967); E. Wasserman, *Prog. Phys. Org. Chem.* **8**, 319 (1971).
33. M. Minato, P. M. Lahti and H. van Willigen, *J. Am. Chem. Soc.* **115**, 4532 (1993).
34. T. Ohana, M. Kaise and A. Yabe, *Chem. Lett.* 1397 (1992).
35. M. Minato and P. M. Lahti, *J. Phys. Org. Chem.* **6**, 483 (1993).
36. K. Itoh, *Pure Appl. Chem.* **50**, 1251 (1978).
37. H. Sixl, R. Mathes, A. Schapp and K. Ulrich, *Chem. Phys.* **107**, 105 (1986).
38. K. Itoh, in *Magnetic Molecular Materials, NATO ASI Series*, edited by D. Gatteschi, D. O. Kahn, J. Miller, and F. Palacio, p. 67. Kluwer, Dordrecht (1991).
39. A. Reiser, H. M. Wagner, R. Marley and G. Bowes, *Trans. Faraday Soc.* **63**, 3162 (1967).
40. D. E. Seeger and J. A. Berson, *J. Am. Chem. Soc.* **105**, 5146 (1983).
41. D. E. Seeger and J. A. Berson, *J. Am. Chem. Soc.* **105**, 5144 (1983).
42. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **107**, 3902 (1985).
43. A. S. Ichimura, K. Ochiai, N. Koga and H. Iwamura, *J. Org. Chem.* submitted.
44. T. Doi, A. S. Ichimura, N. Koga and H. Iwamura, *J. Am. Chem. Soc.* **115**, 8928 (1993).