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

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

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

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

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Abstract: Linkage of two phenylnitrene electron-spin-bearing units by exchange coupling linker groups leads to model open-shell π-conjugated systems of the general structure :N–Ph–X–Ph–N: of various possible connectivity types. Use of variable-temperature electron spin resonance (ESR) spectroscopy of the dinitrenes with cross-conjugating linker groups –X– allowed study of the ground-state spin multiplicities of open-shell systems that are related in a connectivity sense to the theoretically important diradicals trimethylenemethane (–X– = $>C{=}CH_2$, 4,4′-connectivity), oxyallyl (–X– = $>C{=}O$, 4,4′-connectivity), and 1,1,2,3,3-pentamethylenepropane (–X– = $>C{=}CH_2$ or $>C{=}O$, 3,3′-connectivities). For 1,1-bis(4-nitrenophenyl)ethene, a quintet ground state was found with zero-field splitting parameters $|D/hc| = 0.151$ cm^{-1} and $|E/hc| = 0.0029$ cm^{-1}. For the connectivity isomer (*E*)-3,4′-stilbenedinitrene, a quintet ground state with zfs parameters $|D/hc| = 0.146$ cm^{-1}, $|E/hc| = 0.0024$ cm^{-1} was found. For 4,4′-dinitrenobenzophenone, a quintet ground state with zfs parameters $|D/hc| = 0.156$ cm^{-1}, $|E/hc| = 0.0046$ cm^{-1}, was found. For 1,1-bis(3-nitrenophenyl)ethene, a quintet state ESR spectrum was observed, with temperature-dependent intensity behavior that could be fit to a singlet < triplet < quintet states equilibrated model with a singlet ground-state, triplet at −28 cal/mol (−117 J/mol, a negative energy here signifying a low-spin singlet ground state), and quintet at −84 cal/mol (−351 J/mol). For 3,3′-benzophenonedinitrene, a quintet state spectrum was also observed, with temperature-dependent intensity behavior that could be fit by the same model with an ordering of states as follows: singlet ground state, triplet at −16 cal/mol (−67 J/mol), and quintet at −48 cal/mol (−201 J/mol). Overall, the results support the idea that minor heteroatom substitution (such as replacement of a 1,1-ethenediyl unit with a carbonyl unit) need not reverse qualitative connectivity-based exchange coupling effects. The dinitrenes that are disjoint are experimentally found to have low-spin ground states as predicted by the Borden–Davidson model (Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587), but in qualitative disagreement with some simple π-connectivity models (e.g.: Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297).

Introduction

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

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

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[‡] University of Massachusetts, Boston.

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

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

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

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

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

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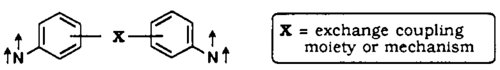
Scheme I



ferromagnetism requires intermolecular exchange as well as intramolecular, the production of high-spin intramolecularly exchange coupled oligomers and polymers is a logical first step in understanding and designing more extensive supramolecular arrays of unpaired electrons. For example, Dougherty has shown the use of the 1,3-cyclobutanediyl unit as a nonconjugated, ferromagnetic coupling linker.[6,7] The groups of Itoh and Iwamura have elegantly shown the ability of *m*-phenylene linking groups to couple carbene units in a ferromagnetic fashion,[8-10] with up to 12 unpaired spins in a system.[11] Our group has carried out fairly extensive computational prediction of the effects of connectivity and other structural features upon the strength and nature of exchange coupling in open-shell systems.[5] Our computations confirm the efficacy of parity-based qualitative models such as those of Ovchinnikov,[12] Klein,[13,14] Mataga,[15] and others[16] in predicting the relationship between π-connectivity and preference for a large variety of high-spin ground states. Despite these and other studies, a very substantial amount of systematic work remains before chemists interested in electronic materials have a dependable "library" relating expected ground-state spin multiplicity to a large number of experimentally attainable molecules and oligomers.

Among our computational studies, we carried out work on the linkage of arylnitrenes by various structural groups. Nitrenes have been much studied, and their electron spin resonance[17] and electronic spectroscopy are fairly well understood. Dinitrenes have been far less studied, aside from the initial work by Wasserman and co-workers[17,18] and a recent study by Iwamura and Murata[19-21] of acetylene- and diacetylene-linked phenylnitrenes. We have for some time felt that the geometric simplicity, synthetic availability, and photochemical lability of dinitrenes make them ideal spin-bearing units in studies of exchange coupling as a function of linker unit –X– (Scheme I). In addition, the work of Wasserman and Iwamura has already shown that the high-spin quintet state of a dinitrene is readily distinguished from low-spin triplet states,[22] and that both are readily distinguished from mononitrene spectra. As a result, we have undertaken to study a number of the dinitrene models described in our original computational studies.

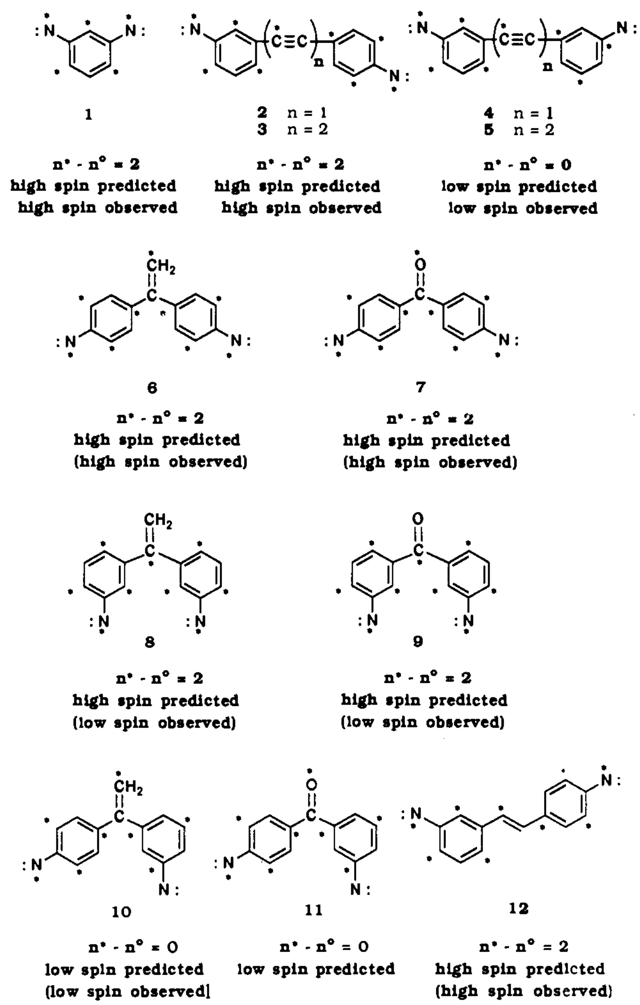


Figure 1. Experimentally observed ground-state multiplicities for some alternant dinitrenes, by comparison to parity-based predictions. n^* = site of α π spin density, n^0 = site of β π spin density. Observed multiplicities in parentheses are from this work; observed multiplicity in brackets for dinitrene **10** is from ref 31.

In this paper, we describe work carried out by our group on phenylnitrene spin-bearing units linked by cross-conjugated linking units, specifically the 1,1-ethenediyl and carbonyl units. We describe the effects of connectivity in these systems and show the difference in exchange behavior between the ethenediyl and carbonyl units. Also, we compare connectivity relationships between the species studied by us and some simpler diradicals of theoretical interest. In the final stages of our work on these systems, we became aware of the work of Professor Hiizu Iwamura's group along lines similar to our study in some respects, which are reported in a paper preceding this one in this issue.

Background

Although dinitrenes have not been extensively studied, two key studies provide sufficient information to use as a definitive starting point in our work. Wasserman and co-workers investigated 1,3-phenylenedinitrene **1**[18] at the same time that they described the corresponding bis(phenylcarbene) (Figure 1). They interpreted the ESR spectral line positions and the strength of the ESR spectrum produced by photolysis of the corresponding diazide at cryogenic temperatures as supportive of a quintet ground state (GS). Iwamura and Murata, working more than 20 years later, described the acetylene and diacetylene linked 3,4′-dinitrenes **2** and **3** as ground-state quintets,[20,21] based upon the similarity of the ESR spectra produced by photolysis of the corresponding diazides to that described by Wasserman, and based upon Curie law analysis of the spectral lines as a function of temperature. In addition, the same study described the related 3,3′-dinitrenes **4** and **5** as having low-spin ground states, based on the temper-

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(6) Jain, R.; Sonsler, M.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356.

(7) Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618.

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

(9) Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Iwamura, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1990**, *112*, 4074.

(10) Itoh, K. In *Magnetic Molecular Materials, NATO ASI Series*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; pp 67.

(11) Nakamura, N.; Inoue, K.; Iwamura, H.; Fujioka, T.; Sawaki, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1484.

(12) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

(13) Klein, D. J. *Pure Appl. Chem.* **1983**, *55*, 299.

(14) Klein, D. J.; Alexander, S. A. In *Graph Theory and Topology in Chemistry*; King, R. B., Rouvray, D. H., Eds.; Elsevier: Amsterdam, The Netherlands, 1987; Vol. 51, p 404.

(15) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 273.

(16) Shen, M.; Sinanoglu, O. In *Graph Theory and Topology in Chemistry*; King, R. B., Rouvay, D. H., Eds.; Elsevier: Amsterdam, The Netherlands, 1987; Vol. 51, pp 373–403.

(17) Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

(18) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

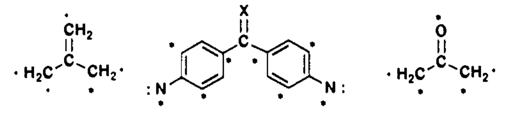
(19) Ichimura, A. S.; Matlin, A. R.; Lahti, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 2868.

(20) Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33.

(21) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

(22) Cf. the related work on quinonoidal triplet dinitrenes: Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526. Singh, B.; Brinen, J. S. *J. Am. Chem. Soc.* **1971**, *93*, 540.

Scheme II



TMM **6** X = CH$_2$ **7** X = O **OA**

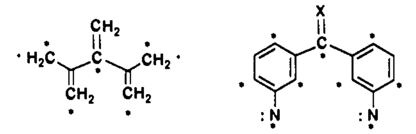
ature-dependent behavior observed for the ESR spectra of these species.

The ground-state multiplicities observed for **1–5** are in accord with the qualitative predictions of π-connectivity or parity-based models variously proposed by Ovchinnikov,[12] Klein,[13] and Mataga.[15] In these models, one may divide an alternant non-Kekulé π-system into alternating sites of α- and β-spin density (designated n^* and n^0, respectively, in the Ovchinnikov model, for example). For any system in which $n^* > n^0$, a high-spin, ferromagnetically exchange coupled ground state is expected; where $n^* = n^0$, a low-spin ground state is expected. Some differences are expected in polycarbenes and polynitrenes by comparison with polyradicals, due to the presence of a band of localized unpaired electrons; as a result, high-spin systems have twice as many unpaired spins as in corresponding polyradicals. As shown in Figure 1, parity-based models predict ground-state spin multiplicities for **1–5** that are in good qualitative accord with experimental evidence.

In previously published work, we computationally studied cross-conjugated dinitrene systems **6–11**,[5] for which ground-state predictions are also shown in Figure 1, based upon the Ovchinnikov model with modification for the presence of nitrene centers as described by Mataga. The high-spin systems **1–3** appear to be well-described by our AM1-CI computational procedure. However, our computations also exhibited an incorrect preference for high-spin states in cases **4** and **5**, where low-spin states are predicted by valence bond considerations[10] and found experimentally by Iwamura and Murata.[20,21] The computed preference for the high-spin quintet in such cases is energetically small by comparison with the large high-spin to low-spin energy gaps in **1–3**, so that we feel the computations confirm the identification of **4** and **5** as weakly exchange coupled, disjoint systems. As a result, our AM1-CI procedure is a practically useful paradigm by which to decide what sorts of organic open-shell π-systems are strongly exchange coupled versus those that are not.

Our interest in cross-conjugated dinitrenes **6–11** is based upon their relationship to some much simpler, fundamental non-Kekulé molecules. Dinitrenes **6** and **7** are related in a connectivity sense to trimethylenemethane (TMM) and oxyallyl (OA), respectively, as shown in Scheme II. TMM and its derivatives have been extensively studied by Dowd[23] and by Berson.[24] It is an archetypal nondisjoint high-spin ground-state diradical, with a triplet–singlet gap of about 15 kcal/mol.[24] All the parity-based models predict it to be a ground-state triplet. OA has the same connectivity as TMM, but (despite suggestions by some parity-based rules that heteroatom substitution should play a role subordinate to connectivity[12] in determining ground-state multiplicity for non-Kekulé molecules) OA appears electronically to be quite different from TMM. Although trapping experiments have implicated OA as a zwitterionic intermediate in a variety of reactions, simple OA derivatives have not been directly observed. Computational studies suggest[19,25] that OA has at most a very small preference for a triplet ground state, and upon minor substitution can become a singlet ground-state species. Given the fact that most substituents do not reverse the ground-state preference of TMM for a triplet, it appears that OA is fundamentally different from TMM despite its similar connectivity. The difference is apparently due to the singular strength of the C=O double bond, which results in carbonyl being a particularly poor exchange coupling linker group.

Scheme III



PMP **8** X = CH$_2$ **9** X = O

We hoped to be able to see whether a qualitative difference in ground-state multiplicity could be observed between **6** and **7**, analogous to the behavior of TMM and OA. An advantage of comparing **6** and **7** is that the low-spin triplet state of **7** could be observed by electron spin resonance (ESR) spectroscopy, whereas the singlet state of OA could not. Earlier AM1-CI computational work by us gave qualitative predictions for exchange linkage of open-shell groups by carbonyl and 1,1-ethenediyl[5] that parallel ab initio computational results for TMM versus OA, as we shall point out in more detail in the Results and Discussion section.

Similar considerations impelled our investigation of dinitrenes **8** and **9**. These two systems differ from **6** and **7** through being disjoint by molecular orbital localizability,[26] despite the π-connectivity based prediction of Figure 1 that these systems should have high-spin ground states. Scheme III demonstrates the disjoint natures of **8** and **9**. A connectivity-related system is 1,1,2,3,3-pentamethylenepropane (PMP), which was suggested by Borden and Davidson to be disjoint by orbital localizability in a similar fashion.[26] Ab initio computations by us[27] support our earlier semiempirical predictions[28] that the triplet state of planar PMP derivatives is the ground state by a small margin. Although we have found evidence permissive of PMP-type intermediate formation in other work,[29] we have not been able to establish experimentally the ground-state spin multiplicity of PMPs. Our investigation of **8** and **9** was intended to see if a high-spin state would be preferred in these disjoint systems, as was predicted to be the case by AM1-CI computations (although the energy gaps between states were not large). AM1-CI calculations found high-spin ground states for the disjoint systems **4** and **5** by 1.2 and 0.1 kcal/mol. These computations were determined to be qualitatively in error by the experimental work of Iwamura and Murata showing the high-spin states to be thermally populated.[20,21] The investigations of **8** and **9** are therefore an additional test for systematic overestimation by our AM1-CI procedure of the relative stability of high-spin states in disjoint conjugated dinitrenes. In addition, they constitute important qualitative tests of the differing ground-state predictions made by the valence-bond based connectivity models[12–14] versus the disjointness criterion.

In order to allow a benchmark for the effect of cross-conjugation versus through-conjugation in closely related dinitrenes, we studied 3,4′-(*E*)-stilbenedinitrene **12**, which is closely related to Iwamura's dinitrene **2**, and to some previously studied stilbene-linked dicarbenes.[30] In this paper, we describe the results of comparing the variable-temperature electron spin resonance spectroscopic behavior of dinitrenes **6–9** and **12**. We do not address the study of the asymmetrically substituted dinitrenes **10** and **11** in this work, but note that dinitrene **10** has been studied by Iwamura and co-workers,[31] and that our work on **11** will be published elsewhere.[32]

Synthesis

All diazide precursors to dinitrenes were synthesized as shown in Figure 2, via diazonium salt formation from appropriate diamino compounds. The synthesis of necessary diamines was fairly straightforward by reduction of the corresponding dinitro com-

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(23) Cf.: Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242.

(24) Cf: Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; John Wiley: New York, 1982; p 151.

(25) Coolidge, M. G.; Yamashita, K.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1751.

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

(27) Ichimura, A. S.; Lahti, P. M. Unpublished results.

(28) Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958.

(29) Kearley, M. L.; Lahti, P. M. *Tetrahedron Lett.* **1991**, *32*, 5869.

(30) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 1266.

(31) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.*, preceding paper in this issue.

(32) Ling, C.; Lahti, P. M. Unpublished results.

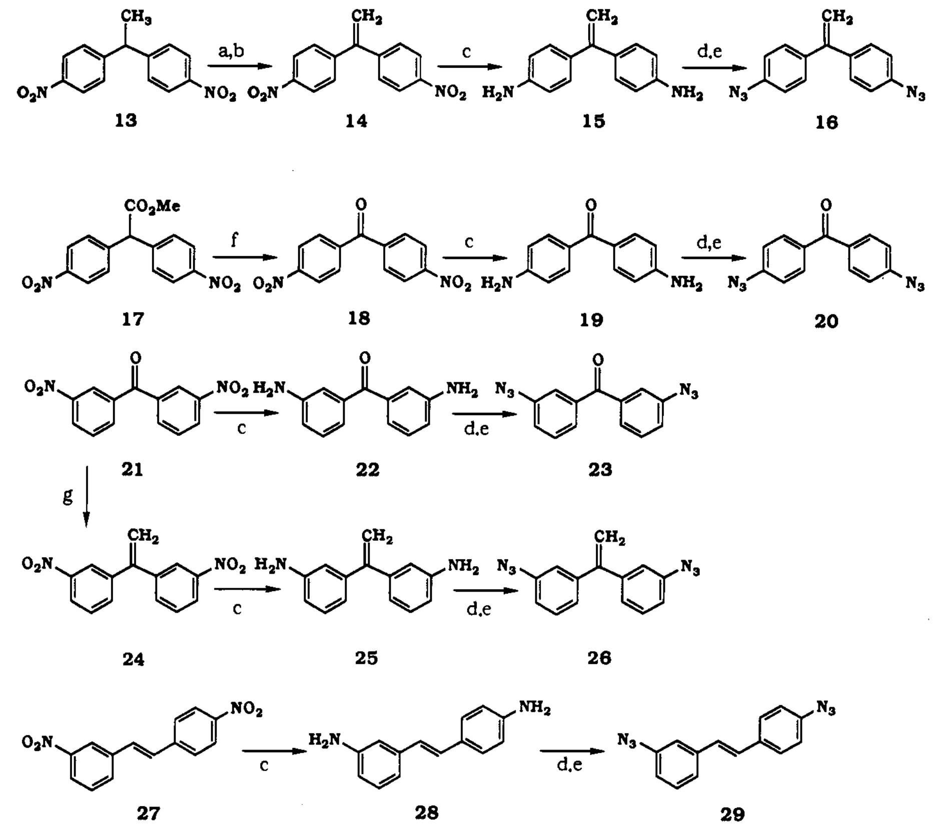


Figure 2. Synthesis of diazide precursors to dinitrenes: (a) *N*-bromosuccinimide, CCl_4, heat; (b) pyridine, reflux; (c) $SnCl_2 \cdot 2H_2O$/EtOH, 70 °C, then neutralize; (d) $NaNO_2$/aq HCl; (e) aq NaN_3; (f) hydrolyze, then CrO_3; (g) $CH_3PPh_3^+Cl^-$/BuLi/THF, then reflux.

pounds, which were available by minor modification of literature procedures described in the Experimental Section.

The resultant diazides were quite stable at room temperature, but were sensitive to fluorescent room lighting or sunlight, turning reddish upon exposure for more than a few minutes. As a result, we stored the diazides at −20 °C in aluminum foil-wrapped vials. Samples remained apparently pure under these conditions after several months.

Computational Methods

Computational results described in this paper are obtained using the AM1-CI procedure described in our earlier work.[5] Any differences between the numbers given in this present work versus those found previously are due to minor refinements in selection of interacting configurations for calculations of state energy gaps for a given molecule. All qualitative state orderings were found to be the same as those found previously,[5] even where energetic gaps between states changed somewhat.

Results and Discussion

I. Photolysis Considerations. All diazide samples were photolyzed at temperatures between 60 K and 77 K, and maintained at this temperature for 15 min before analyzing the ESR spectral behavior. Previous work has shown that diazide photolysis at very low temperatures must be followed by annealing at 65 K to achieve usefully reproducible Curie law data. Without the annealing step, we (like Murata and Iwamura[21]) found that 12 K photolysis followed by stepwise warming led to a sudden, irreversible *increase* in the dinitrene spectral peaks in the 55–65 K temperature range. Such irreversible behavior upon annealing was attributed[21] to equilibration of a range of dinitrene conformers produced in rigid matrix conditions upon very-low-temperature photolysis, as would be plausible upon slight softening of the 2-methyltetrahydrofuran matrix at higher temperatures. However, our procedure of photolyzing at higher temperatures gave reproducible thermal behavior without the need for an extra annealing step. All spectra decayed and disappeared irreversibly at temperatures greater than about 85–90 K, at which point the frozen 2-methyltetrahydrofuran would be expected to become more permeable to molecular motion.

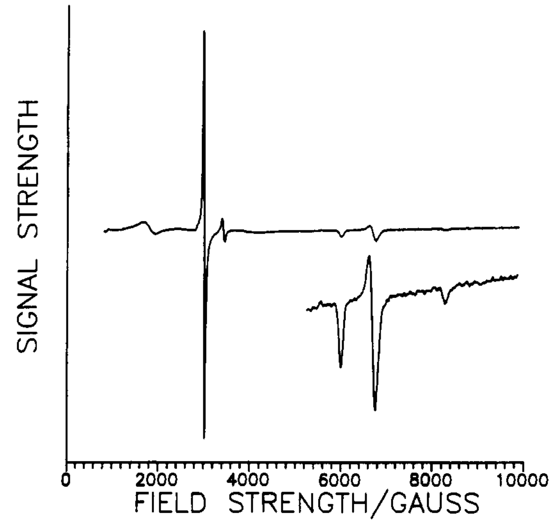


Figure 3. ESR spectrum from photolysis of diazide **16** in 2-methyltetrahydrofuran at 77 K at 9.34 GHz: abscissa in units of gauss (10 G = 1 mT), ordinate scaled to the figure size from the original digitized spectrum. Peak assignments are given in the text.

II. 1,1′-Bis(4-phenylnitreno)ethene and 3,4′-Stilbenedinitrene. Photolysis for 5 min through a Pyrex filter of diazide precursor **16** in degassed 2-methyltetrahydrofuran frozen matrix at 77 K gave a strong quintet ESR spectrum attributable to **6**, shown in Figure 3. Photolysis using an Oriel 300–400-nm band pass filter, or using the 308-nm light of a xenon chloride excimer laser, also gave essentially the same spectrum. Very little radical impurity peak at about 3400 G was observed in photolysis of **16**, if the sample was passed through a plug of alumina prior to irradiation. The strong peak at 3005 G is definitive for a quintet multiplicity, in conjunction with the weak high-field peak at 8270 G attributable[18] to the H_1 transition. We assume that the peaks at 8270 and 5990 G are the highest field two peaks for the quintet **6**. Using the procedure described by Wasserman[18] for these peaks, the

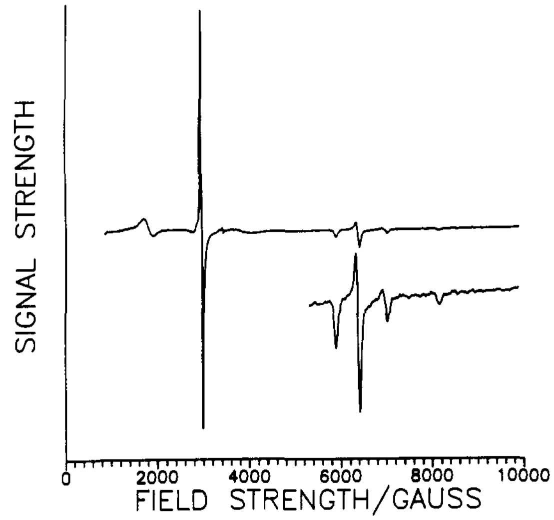


Figure 4. ESR spectrum from photolysis of diazide **29** in 2-methyltetrahydrofuran at 77 K at 9.34: abscissa in units of gauss (10 G = 1 mT), ordinate scaled to the figure size from the original digitized spectrum. Peak assignments are given in the text.

Table I. Electron Spin Resonance Spectroscopic $|D/hc|$ Values for Selected Quintet Dinitrene Spectra

compd	$\|D/hc\|^a$	compd	$\|D/hc\|^a$
1	0.162^b	**6**	0.151^d
2	0.157^c	**7**	0.156^d
3	0.157^c	**12**	0.146^d

$^a|D/hc|$ given in cm^{-1}, where 1 cm^{-1} = 10 700 G = 1070 mT. ^{b}Reference 18 and 21. ^{c}Reference 21. ^{d}This work.

zero-field splitting (zfs) parameters for quintet **6** are approximately $|D/hc| = 0.151$ cm^{-1} and $|E/hc| = 0.0029$ cm^{-1} (0.093 48 cm^{-1} = 1000 G).[33] A single, modest-sized peak at 6675 G in Figure 3 is attributable to a triplet mononitrene with $|D/hc| = 0.938$ cm^{-1}, derived from photocleavage of a single azide moiety.[18]

As a test of parity considerations in controlling the ground-state spin multiplicities of nondisjoint systems, we compared the spectrum of **6** to that of the isomeric species **12**. Photolysis of diazide **29** gives **12** with a very strong, nearly identical spectrum (Figure 4) to that of **6**, with two residual triplet mononitrene peaks at 6360 G and 6975 G ($|D/hc| = 0.822$ and 1.053 cm^{-1}), attributable to photolysis of the azide moieties attached in the 4′- and 3-positions, respectively. The upfield shift of the 4′-position nitrene peak relative to that in the 3-position is consistent with the effects of resonance interactions with the stilbene ethylenic unit. As with **16**, only a minor radical peak at ca. 3400 G was produced, but a strong, distinctive quintet peak is observed at 2970 G. From the peaks at 8110 and 5880 G, the zfs values for **12** are estimated[33] to be $|D/hc| = 0.146$ cm^{-1} and $|E/hc| = 0.0024$ cm^{-1}. Iwamura has pointed out that, in strongly interacting cases such as **6** and **12**, theoretical arguments relating the vector angle between the two interacting C–N centers to the observed $|D/hc|$ zfs parameter in quintet dinitrenes are not necessarily expected to hold true.[21] However, for **6** (and **7**, as we shall see below) as for systems **2** and **3**, the vector angle between C–N centers in any conformer must be about 120°, and $|D/hc|$ values in all of these systems are remarkably similar, despite fairly substantial structural differences. Table I summarizes $|D/hc|$ zfs parameters for these nondisjoint quintet dinitrenes. Dinitrene **12** also fits the trend with a 120° vector angle between interacting C–N centers, although the *E*-ethylenic linking group complicates, somewhat, comparison to the others.

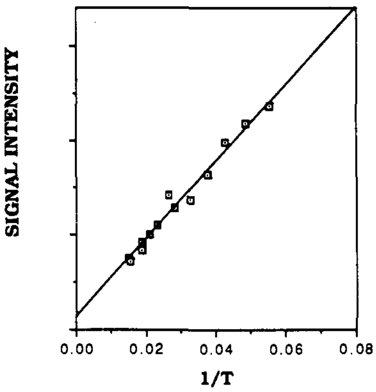


Figure 5. Curie plot for the peak at 3005 G in Figure 3. Abscissa is in units of reciprocal absolute temperature (K^{-1}); ordinate is relative intensities of 3005 G peak at the various temperatures.

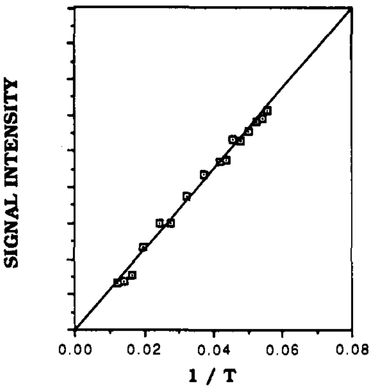
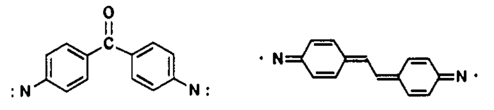


Figure 6. Curie plot for the peak at 2970 G in Figure 4. Abscissa is in units of reciprocal absolute temperature (K^{-1}); ordinate is relative intensities of 2970 G peak at the various temperatures.

Scheme IV



7 30

Curie law plots of quintet ESR signal intensity as functions of reciprocal absolute temperature for dinitrenes **6** and **12** are shown in Figures 5 and 6. As far as may be analyzed from the linearity of these plots, both are consistent with a quintet ground state. AM1-CI semiempirical molecular orbital computations by us have predicted the quintet–triplet gaps in **6** and **12** to be 8.5 and 4.0 kcal/mol,[5] respectively, indicating that these are strongly exchange-coupled quintets that are expected to have linear Curie behavior. The formal possibility has been discussed elsewhere that linear Curie plots may be observed for cases of exact degeneracy between ESR-active and ESR-inactive states,[34] or for cases where a kinetically stable ESR-active state is produced that cannot relax to a thermodynamically lower state.[35] Our computational studies of **6** and **12**, and the qualitatively nondisjoint nature of these systems, lead us to argue that both of these dinitrenes are ferromagnetically coupled, high-spin molecules, with substantial energy gaps to excited states of lower multiplicity. Topologically, these systems are therefore related, in spite of their substantially different connectivity.

III. 4,4′-Benzophenonedinitrene. Photolysis of diazide **20** at 77 K produced the ESR spectrum shown in Figure 7. The peaks at 3030 and 8445 G are consistent with the quintet state of dinitrene **7** having zfs parameters of $|D/hc| = 0.156$ cm^{-1} and

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[33] In Wasserman's[18] original procedure it was assumed that the quintet peak for **1** of second highest field was obscured by mononitrene peaks in the region of 6000–7000 G. This procedure was also followed by Murata and Iwamura in calculating $|E/hc|$ values for quintets **2** and **3**.[20,21] If we assume that this is also true for our quintet ground-state dinitrenes, we compute essentially the same $|E/hc|$ value of 0.017 cm^{-1} for **6**, **7**, and **12**.

[34] Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley: New York, 1988; Vol. 2, pp 462–469.

[35] Reynolds, J. H.; Berson, J. A.; Kumashiro, K.; Duchamp, J. C.; Zilm, K. W.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 763.

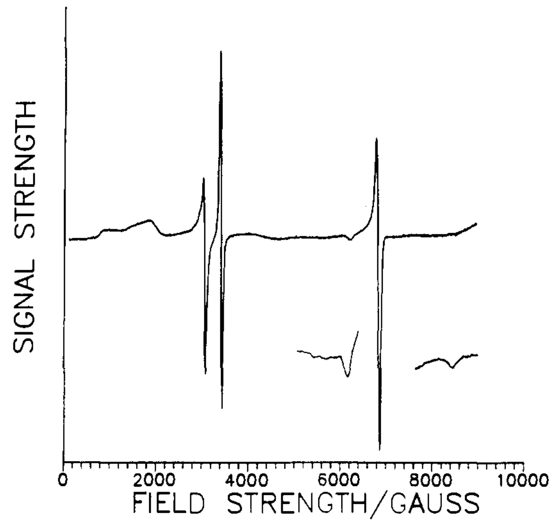

Figure 7. ESR spectrum from photolysis of diazide **20** in 2-methyltetrahydrofuran at 77 K at 9.34 GHz: abscissa in units of gauss, ordinate scaled to the figure size from the original digitized spectrum. Peak assignments are given in the text.

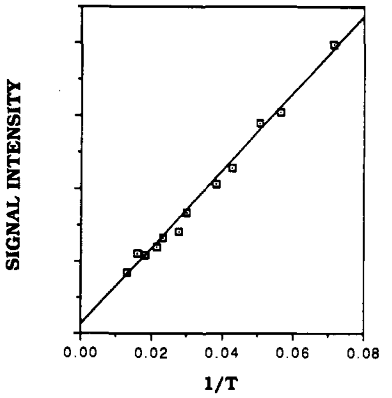

Figure 8. Curie plot for the peak at 3030 G in Figure 7. Abscissa is in units of reciprocal absolute temperatures (K^{-1}); ordinate is relative intensities of 3030 G peak at the various temperatures.

$|E/hc| = 0.0046\ \text{cm}^{-1}$ (Table I). However, the quintet spectrum was substantially weaker by comparison to the mononitrene remnant at 6755 G ($|D/hc| = 0.968\ \text{cm}^{-1}$) than was observed for photolysis of **16**. A substantial amount of monoradical impurity peak was produced in the 3400-G region, regardless of the wavelength of light used for irradiation, or whether the sample was passed through alumina prior to irradiation. Reiser et al.[36] reported in a UV–vis spectral study of several dinitrenes that photolysis of diazide **20** gave production only of a mononitrene UV–vis spectrum, as far as they could observe. However, these workers studied a set of dinitrenes that would give rise to localized quinonoidal dinitrenes such as **30** (Scheme IV), except in their photolysis of ketone **20**, which cannot give a quinonoidal dinitrene. It is not clear, therefore, that the UV–vis spectrum of **7** should be similar to those of quinonoidal dinitrenes such as **30**. Our ESR investigation can readily distinguish quintet dinitrene **7** from other multiplet states and from mononitrene products of partial photolysis, while a UV–vis study could not easily probe such distinctions by inspection.

A Curie law plot of the quintet ESR signal at 3030 G as a function of reciprocal absolute temperature for dinitrene **7** is shown in Figure 8. As far as may be analyzed from the linearity of this plot, dinitrene **7** appears to have a quintet ground state, as does the π-isoanalogue **6**. We were somewhat surprised by this result, since computational work (vide supra) by ourselves[19] and by Coolidge et al.[25] has suggested that the carbonyl group is a poor exchange linking group. Whereas trimethylenemethane has been computed at a fairly high level of computation to have a triplet ground-state preference by ca. 15 kcal/mol,[37] comparable computations for unsubstituted oxyallyl find a triplet preference by only ca. 1–2 kcal/mol.[25] These results are similar to the related quintet–triplet gaps computed at the AM1-CI level for **6** and **7**, which are 8.5 and 0.4 kcal/mol, respectively; these values suggest a smaller exchange coupling between unpaired electrons in the π-orbitals of carbonyl-linked **7** than in hydrocarbon-linked **6**.

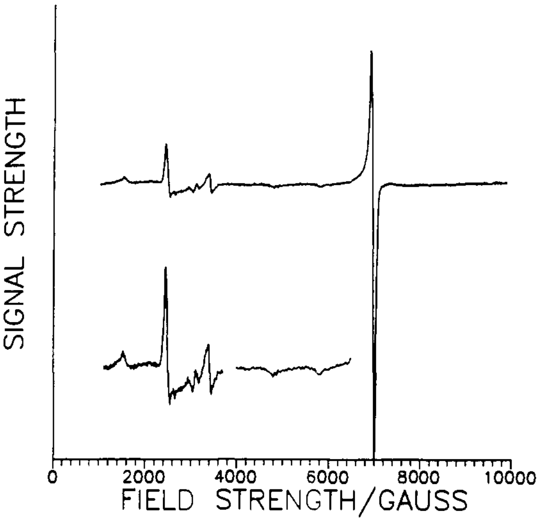

Figure 9. ESR spectrum from photolysis of diazide **26** in 2-methyltetrahydrofuran at 77 K at 9.44 GHz; abscissa in units of gauss, ordinate scaled to the figure size from the original digitized spectrum. Peak assignments are given in the text.

As a result of computational work, we have a reason to expect that **6** and **7** have strikingly different magnitudes of exchange coupling between the linked two dinitrene centers. Unfortunately, our experimental results could be described by at least three situations, even if we *assume* that the high-spin to low-spin gap in quintet **6** is large (≥ 10 kcal/mol): (1) the exchange coupling in **7** is of comparable magnitude to that in **6**; (2) the exchange coupling in **7** is substantially smaller (1–2 kcal/mol) than that in **6**, but still sufficiently large to give a linear Curie plot; (3) the exchange coupling in **7** is so small that the quintet and singlet states are virtually degenerate, again giving a linear Curie plot. There is not even any experimental justification for assuming that the exchange coupling in **6** is "large", save by comparison to computational results.

As a result, we are left with a certain degree of dissatisfaction concerning the interpretation of the experimental results for **7**, due to the inherent limitations of the Curie plot method for evaluating ground-state multiplicity. Based upon computational evidence, we suspect that **7** actually favors a high-spin ground state by a modest (1–3 kcal/mol) energetic margin sufficient to give linear Curie law behavior, while **6** favors the high-spin state by a rather larger amount. However, we cannot prove this by presently used experimental methodology.

IV. **1,1-(3-Phenylnitreno)ethene.** Photolysis of the disjoint 1,1-ethenediyl diazide precursor **26** to dinitrene **8** at 77 K yielded the ESR spectrum shown in Figure 9. Aside from the monoradical impurity peak at about 3400 G, the spectrum is dominated by the mononitrene peak at 6950 G ($|D/hc| = 1.013\ \text{cm}^{-1}$), although smaller peaks are observed at 1520, 2445 (moderate), 3130, 4810, and 5810 G. Except for the peak at 2445 G, the latter peaks are quite weak in intensity. The disjoint dinitrenes **4** and **5** described earlier had ESR peaks at 150, 2720, 3110, and 8600 G (very weak).[21] Differences in relative peak intensities and positions between **4–5** and **8** seem reasonably attributable to differences in connectivity between the weakly exchange coupled **4** and **5** versus **8**. Murata and Iwamura observed a small, tem-

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(36) Reiser, A.; Wagner, H. M.; Marley, R.; Bowes, G. *Trans. Faraday Soc.* **1967**, *63*, 3162.

(37) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; John Wiley: New York, 1982; pp 173 ff.

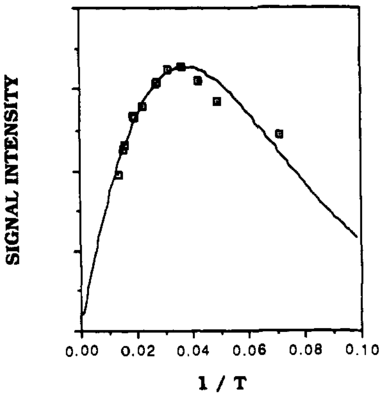


Figure 10. Curie plot for the peak at 2445 G in Figure 9. Abscissa is in units of reciprocal absolute temperature (K^{-1}); ordinate is relative intensities of the 2445 G peak at the various temperatures.

perature-dependent peak at 2370 G for both **4** and **5** that they attributed to the triplet state of these systems, due to its qualitatively different temperature dependence by comparison to the assigned quintet peaks. We could not identify any peaks clearly attributable to a triplet state of **8** in the photolysate of **26**, although there were some low-temperature changes in the appearance of the extreme high-field wing of the 2445-G peak.

The absence of a small peak at >8000 G in the spectrum of Figure 9 may be due to the fact that this transition is simply too weak to observe, in which case we are unable to estimate the zfs parameters for quintet **8**. However, if we assume that the two peaks at 4810 and 5810 G are the two highest field transitions of the quintet, we find by our earlier-used procedure zfs parameters of $|D/hc| = 0.077\ \text{cm}^{-1}$ and $|E/hc| = 0.030\ \text{cm}^{-1}$. While this peak assignment must be considered quite uncertain at present, if correct it would imply a substantially reduced zfs relative to values for disjoint nitrenes **4** and **5**,[21] possibly due to conformational effects in **8** (and its analogue **9**) that are considered below.

A high-spin ground state was predicted for **8** by 4.6 kcal/mol with our earlier AM1-CI computational methods,[5] while more recent results with different CI active spaces but retaining a planar geometry give qualitatively the same result but with a quintet-singlet gap reduced to 1.6 kcal/mol and a quintet–triplet gap of 2.7 kcal/mol. The computed gaps are not greatly affected by comparison of the three possible planar isomers of **8** with the C–N bonds in different orientations. Figure 10 shows a Curie plot of the experimental ESR intensity of the peak at 2446 G as a function of reciprocal temperature. A substantial concave-down curvature is found in this plot, which may be fit to eq 1 that has been

$$I = (C/T)([5\exp(-6J/RT)]/[5\exp(-6J/RT) + 3\exp(-2J/RT) + 1]) \quad (1)$$

formulated in previous work[21] to model the relative state energies in a system consisting of a pair of weakly interacting carbenes or nitrenes. Equation 1 describes the Curie intensity behavior of a spin-equilibrated system consisting of a ground-state singlet, and excited-state triplet and quintet states $2J$ and $6J$ higher in energy. T is absolute temperature, and C is a constant chosen to fit the arbitrary relative intensity scale used to measure the variation in peak intensity. A nonlinear least-squares fit of the data for Figure 10 to eq 1 yields a value of $J = -13.6 \pm 1.6$ cal/mol at a 95% confidence level (with the negative value signifying a low-spin singlet ground state), corresponding to a triplet state at −28 cal/mol and a quintet state at −84 cal/mol. Although we could not directly observe any ESR signals attributable to triplet dinitrene **8**, the fairly good fit of eq 1 to the data of Figure 10 encourages us to feel that the model for eq 1 is a reasonable one to use, in the absence of a clearly better model.

This result is in qualitative disagreement with our AM1-CI results for a planar system **8**, which predict a quintet ground state by a small margin in accord wtih valence bond expectations. However, the finding of a singlet ground state is in accord with Borden and Davidson's criteria for disjoint open-shell systems, and with findings of singlet ground states for disjoint dicarbenes[8,10] and the disjoint acetylene and diacetylene linked dinitrenes **4** and **5** mentioned earlier. For **4** and **5**, experiments found that J was −30 to −35 cal/mol, and −15 to −20 cal/mol, respectively, with the singlet, triplet, and quintet states described as being in ascending energetic order according to eq 1.[21]

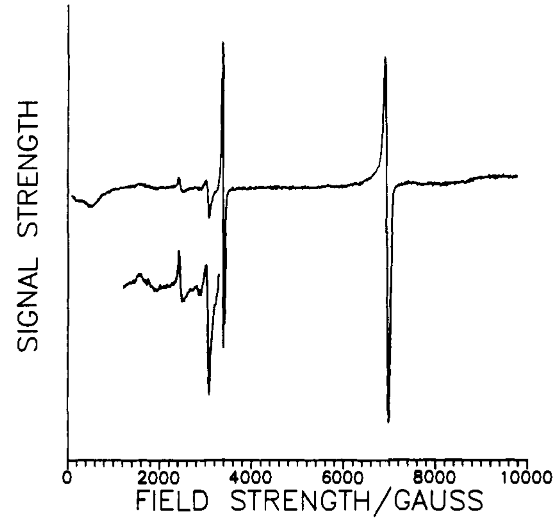
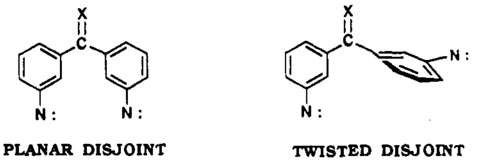


Figure 11. ESR spectrum from photolysis of diazide **23** in 2-methyltetrahydrofuran at 77 K at 9.34 GHz: abscissa in units of gauss, ordinate scaled to the figure size from the original digitized spectrum. Peak assignments are given in the text.

Scheme V



The qualitative finding of a singlet ground state for **8** may be due to a twisted geometry of one or both phenylnitrene units relative to the nominally conjugating 1,1-ethenediyl linking moiety (Scheme V). Such twisting would reduce the amount of exchange possible between the electrons in the system and probably lower any triplet–singlet splitting. Of course, it is quite possible that the singlet is inherently the ground state even in a planar situation. However, given the results of our semiempirical computations upon planar **8**, and the small high-spin triplet preference found for planarized pentamethylenepropane derivatives at ab initio post-Hartree–Fock levels of theory,[27] we feel that a planar-constrained version of the connectivity type represented by **8** will be needed to help to settle this point.

V. 3,3′-Benzophenonedinitrene. Photolysis of the disjoint ketene diazide precursor **23** to dinitrene **9** at 77 K produced the ESR spectrum shown in Figure 11. While fairly weak relative to the radical peak at about 3400 G and the mononitrene remnant at 6495 G ($|D/hc| = 1.037\ \text{cm}^{-1}$), peaks at 1550 (very weak), 2420, and 3040 G attributable to the quintet state of **9** are readily observable. In combination with the results for the nondisjoint diazide precursor **20**, it seems that the carbonyl linked diazides give less dinitrene relative to mononitrene for a given photolysis time than do the 1,1-ethenediyl linked diazides. The two peaks at 2420 and 3040 G attributed to **9** are fairly comparable in both position and intensity to some of those described earlier for the disjoint dinitrenes **4** and **5** studied in previous work. Possible high-field (>4000 G) peaks expected for **9** are so small as not to be seen, so we could not estimate the zfs parameters for **9**. The weak intensities of high-field peaks for the carbonyl linked dinitrenes **7**, **9**, and **11**[32] appear to be general, by comparison to corresponding peaks for the analogous 1,1-ethenediyl linked dinitrenes. In addition, no clear evidence for peaks corresponding to triplet dinitrenes was obtained in our experiments.

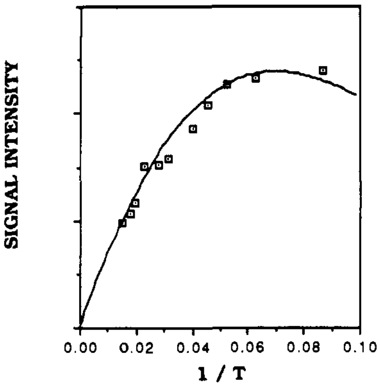
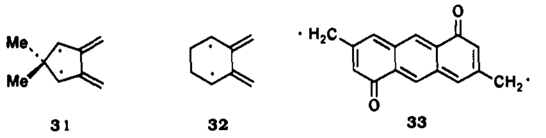


Figure 12. Curie plot for the peak at 2420 G in Figure 11. Abscissa is in units of reciprocal absolute temperature (K^{-1}); ordinate is relative intensities of the 2420 G peak at the various temperatures.

Scheme VI



AM1-CI computations for **9** find degenerate quintet and triplet states to within <0.1 kcal/mol, and a quintet to singlet gap of 0.5 kcal/mol. This finding is consistent with the computational work described earlier to justify the poor efficacy of the carbonyl group in exchange coupling. In addition to the poor natural exchange ability inherent in its carbonyl linking group, system **9** is also disjoint by the Borden–Davidson criteria and is expected to have a very small gap between high-spin and low-spin states. Figure 12 shows the Curie plot data for the 2420-G peak of the spectrum in Figure 11. The concave-down curvature is far less pronounced than in Figure 10, but may still be fit to eq 1 for weakly coupled nitrene states, as described in the previous section. Nonlinear least-squares analysis of the data yields $J = -8.0 \pm 0.8$ cal/mol at 95% confidence, corresponding to a triplet state at −16 cal/mol and a quintet state at −48 cal/mol, again with negative numbers signifying a singlet ground state. Although our AM1-CI results qualitatively predict a quintet ground state for **9**, the computed gap is so small that we feel this result to agree well with the experimental result, since both experiment and theory are consistent with a system in which coupling exists just sufficient to produce a set of nearly degenerate states, in which small geometric or substituent effects could cause reordering of the states relative to one another. Also, the smaller exchange coupling magnitude (singlet–quintet gap) for **9** by comparison to that for **8** provides the first experimental evidence to our knowledge in support of arguments that the carbonyl group is a less effective exchange coupling unit than is the 1,1-ethenediyl group. With this minor difference, both cross-conjugated 3,3′-connectivity systems are qualitatively disjoint in nature.

The combination of our results and those of Itoh et al.[10] and Iwamura et al.[20,21] therefore suggests that the disjointness criterion is effective at modeling the ground-state multiplicities for conjugated dinitrenes and dicarbenes. It remains unclear why a number of disjoint di*radical* systems such as tetramethyleneethane[38] and its conformationally constrained analogues **31** and **32**[39,40] and Berson's diradical **33**[41,42] (Scheme VI) appear to have high-spin triplet ground states, when so many disjoint dinitrene and dicarbene systems have low-spin ground states.

Table II. Comparison of AM1-CI and Experimental Energy Gaps for Dinitrenes **2–9** and **12**

compd	AM1-CI $\Delta E_{Q\text{-}T}{}^{a}$	exptl $\Delta E_{Q\text{-}S}{}^{a}$
2	2700	>1000[c]
3	2000	>1000[c]
4[b]	1200	−33[c,e]
5[b]	110	−17[c,e]
6	8500	>1000[d]
7	340	>1000[d]
8[b]	2700	−84[d]
9[b]	80	−48[d]
12	4000	>1000[d]

[a] Energy gap ΔE in cal/mol; theoretical numbers determined by AM1-CI as in ref 5, experimental numbers determined as referenced. A negative number denotes a low-spin ground state. A value >1000 cal/mol denotes a linear Curie plot of ESR signal intensity and is subject to caveats described in the text and in ref 34. [b] Denotes a connectivity disjoint system as defined in ref 26. [c] Reference 21. [d] This work. [e] A typical value for a range of different rotamers is given.

Conclusions

We find dinitrenes coupled by conjugated linking groups (:NPh–X–PhN:) to be very useful in evaluating the qualitative relationships between structure and exchange coupling in organic open-shell systems. While the dinitrenes have complications in attempting detailed ESR spectral interpretation, the broad range of their spectra, ease of cryogenic nitrene center generation, and ease of differentiating mononitrene from dinitrene peaks makes these systems very useful in investigating models for organic magnetic materials. In addition, diazide dinitrene precursors are fairly readily synthesized, handled, and stored. A variety of other linking groups –X– in dinitrene model systems are being investigated in our labs, and will be reported upon in due course.

Table II summarizes a comparison of experimental results with AM1-CI computational predictions for dinitrenes **2–9** and **12**. We compare computed quintet–triplet gaps to experimental quintet–singlet gaps, since quintet–triplet gaps are more reliably computed, and quintet–singlet gaps are more readily measured. Although computational chemistry has suggested that the effect upon exchange coupling between unpaired electrons of replacement of a 1,1-ethenediyl linking group with a carbonyl group will be substantial, we found that for the systems studied, the effects of connectivity were *qualitatively* dominant. Both nondisjoint dinitrenes were found to be ground-state species, although the relative sizes of the quintet to low-spin state energy gaps could not be determined (as is generally true in such studies) due to the limitations of Curie law experiments. Both disjoint dinitrenes were found to have nearly degenerate ground states, with singlet ground states favored by <100 cal/mol over ESR-active quintet states, in qualitative accord with Borden and Davidson's formulation for disjoint systems.

The results for the disjoint cases in particular suggest that the AM1-CI semiempirical computational procedure (used by us in previous studies aimed at defining important model open-shell systems) incorrectly favors high-spin states of disjoint dinitrenes over low-spin, so that a small preference for the quintet state is predicted, while a small preference for the singlet is observed. As a result, it is important to consider such AM1-CI predictions strictly in the spirit that they were presented in publication, namely, as a method to classify open-shell systems as robust triplets, robust singlets, and systems with states that are near-degenerate, rather than basing experimental courses of action on the energetic magnitudes of any single AM1-CI result, especially for a disjoint system. Further investigation will be required to decide if the qualitative failure of computational theory to describe the ground-state multiplicities of **4–5** and **8–9** is due to effects secondary to connectivity (such as geometric torsion), or to more fundamental limitations of the semiempirical procedure used by us.

Experimental Section

General. Unless otherwise described below, all reagent chemicals were used as received from Aldrich Chemical Co. 2-Methyltetrahydrofuran was distilled from calcium hydride and tetrahydrofuran from potassi-

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(38) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.

(39) Roth, W. R.; Kowalcik, U.; Maier, G.; Reisenauer, H. P.; Sustman, R.; Mueller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1285.

(40) Dowd, P.; Chiang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1987**, *109*, 5284.

(41) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5146.

(42) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251.

um/benzophenone, both under argon.

All melting points described below are uncorrected. Ultraviolet–visible spectra were obtained on a Shimadzu UV-260 double-beam spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1420 spectrophotometer and were referenced against polystyrene at 1601 cm^{-1}. ^1H NMR spectra were obtained on an IBM Instruments NR-80A Fourier transform spectrometer and were referenced against internal tetramethylsilane on the delta (δ) scale in parts per million. Chemical analyses were performed by the University of Massachusetts Microanalytic Laboratory.

Electron spin resonance (ESR) spectra were obtained on either a Bruker ESP-300 X-band spectrometer attached to a standard Bruker data system allowing multiscan spectral digitization and analysis or on a Varian E-9 X-band spectrometer attached to hardware allowing multiscan spectral digitization and analysis with ASYST software. ESR peak positions are reported in units of gauss; peak intensities were obtained by computer-aided double integration using standard Bruker software routines. ESR line positions were calibrated relative to solid diphenylpicrylhydrazyl radical ($g = 2.0037$) for the ESP-300, while spectrometer frequency ν_0 was measured by a microwave counter on the E-9.

1,1-Bis(4-nitrophenyl)ethane (13). 1,1-Diphenylethane (15.8 g, 0.087 mol) was added slowly to a vigorously stirred solution of 90 mL of fuming nitric acid and 7.5 mL of water, while maintaining the reaction temperature below 5 °C. After addition, the reaction was allowed to warm to room temperature with stirring overnight. The clear orange solution was poured onto water and extracted with benzene. The organic layer was dried and evaporated to leave an orange oil, which partially solidified upon standing. The supernatant oil was decanted, and the remaining solid recrystallized twice from absolute ethanol to give 9.2 g (39%) of pale yellow crystals of **13**, mp 105–107 °C (lit.[43] 110.5–112 °C).

1,1-Bis(4-nitrophenyl)ethene (14). Compound **13** (2 g, 7.3 mmol) was heated under reflux with a sun lamp in 100 mL of carbon tetrachloride containing *N*-bromosuccinimide (4.0 g, 22.5 mmol) and 140 mg of benzoyl peroxide. After 165 min, the reaction was allowed to cool and was filtered. The organic solution was evaporated and the residue heated under reflux in 30 mL of dry pyridine for 75 min. The reaction was then allowed to cool and poured into water. The crude brown solid product was collected, dried, and then recrystallized from methanol (with charcoal decolorization) to give 0.84 g (42%) of **14**, mp 173–175 °C (lit.[43] mp 175–176.5 °C).

1,1-Bis(4-aminophenyl)ethene (15). A solution of 0.67 g (3 mmol) of **14** and 6.67 g (30 mmol) of stannous chloride dihydrate in 15 mL of absolute ethanol was heated at 70 °C for 30 min under nitrogen, allowed to cool, and poured onto ice. The milky white solution was neutralized with 10% aqueous sodium bicarbonate to a pH of 7–8. The resulting basic mixture was extracted with dichloromethane, and the organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated to give a pale yellow solid. The crude product was dissolved in dichloromethane, treated with activated charcoal, and filtered. Evaporation of the solvent gave 0.5 g (96%) of yellow solid **15**, mp 169–171 °C (lit.[44] mp 170–172 °C). IR (KBr; cm^{-1}) 3440 and 3400 (NH_2 str), 3330 and 3200 (C–H str), 895 (m, $=CH_2$). ^1H NMR ($CDCl_3$, 80 MHz; ppm) δ 6.63–7.17 (para AA′BB′ q, 8 H, $J = 8.5$ Hz), 5.24 (s, 2 H), 3.69 (br s, 4 H).

1,1-Bis(4-azidophenyl)ethene (16). To 0.29 g (1.4 mmol) of **15** were added 1.1 mL of water and 0.6 mL of concd HCl. The mixture was cooled to 0 °C and treated slowly dropwise with a solution of 0.20 g (3 mmol) of sodium nitrate in 0.7 mL of water, and then stirred for 1.5 h at 0–5 °C. To the clear orange solution was added 0.18 g (3 mmol) of sodium azide in 0.7 mL of water. The reaction mixture was stirred for 15 min, then extracted with dichloromethane. The organic extract was treated with charcoal, then anhydrous magnesium sulfate, and filtered. Removal of the solvent gave 0.25 g (69%) of golden yellow solid **16**, mp 101–103 °C. Anal. Calcd: C, 64.1; H, 3.8; N, 32.0. Found: C, 62.0; H, 3.9; N, 31.5. IR (KBr, cm^{-1}) 2133 (str, N=N=N str), 905 (m, $=CH_2$). ^1H NMR (acetone-d_6, 80 MHz) δ 7.1–7.4 ppm (para AA′BB′ q, 8 H, $J = 8.6$ Hz), 5.48 (s, 2 H). UV-vis λ_{max} (ϵ, M^{-1} cm^{-1}) 272 nm (47 500).

Methyl 2,2-Bis(4-nitrophenyl)ethanoate (17). Over 45 min, 4 g (17.7 mol) of powdered methyl diphenylethanoate was added to 40 g of well-stirred fuming nitric acid, while maintaining the temperature below 30 °C. After addition was complete, the mixture was stirred at room temperature for 4.5 h, then poured onto ice. The resulting solid was separated, dissolved in ethyl ether, and washed with saturated aq sodium bicarbonate, water, and brine. After the organic layer was dried and evaporated, the crude solid product was recrystallized twice from glacial acetic acid and once from ethanol to give nearly white crystalline **17**, yield 0.9 g (16%), mp 165–166 °C (lit.[45] mp 165.5–166.7 °C).

4,4′-Dinitrobenzophenone (18). Following the procedure of Hunsberger and Amstutz,[45] ester **17** (9 g, 29 mmol) was boiled for 18 h in 230 mL of glacial acetic acid, 5 mL of concd sulfuric acid, and 50 mL of water. The reaction was poured onto ice and filtered; the solid was rinsed with water. Upon drying, 6.2 g (72%) of crude 2,2-bis(4-nitrophenyl)ethanoic acid, mp 147–150 °C dec (lit.[45] 166.4–169.6 °C), was obtained, with purity sufficient for the next step.

The 2,2-bis(4-nitrophenyl)ethanoic acid (6 g, 20 mmol) was then boiled with chromium trioxide (12.2 g, 120 mmol) in 240 mL of glacial acetic acid for 21 h, and poured onto ice. The resultant solid was collected, washed thoroughly with water, and recrystallized twice from glacial acetic acid and once from ethanol to give 2.8 g (50%) of pale cream-colored solid **18**, mp 189–193 °C (lit.[45] mp 189.6–190.6 °C).

4,4′-Diaminobenzophenone (19). A solution of ketone **18** (1.64 g, 6 mmol) and stannous chloride dihydrate (13.5 g, 60 mmol) in 35 mL of ethanol was heated at 70 °C for 45 min under nitrogen. The resultant clear orange solution was allowed to cool and poured onto ice, then neutralized with 10% aq sodium bicarbonate to pH 8. The milky white solution was extracted with warm ethyl acetate. The organic extract was washed with water and brine and dried; the solvent was evaporated to give 1.2 g (66%) of yellow, powdery **19**, mp 244–246 °C (lit.[46] mp 241 °C).

4,4′-Diazidobenzophenone (20). Diamine **19** (0.50 g, 2 mmol) was dissolved in 2 mL of water containing 1.1 mL of concd HCl, and cooled to 0 °C, then treated dropwise with a solution of sodium nitrite (0.34 g, 5 mmol) in 1.2 mL of water. After the addition, the reaction was maintained at 0–5 °C for 1 h. To the resultant clear orange solution was added dropwise 0.31 g (5 mmol) of sodium azide in 1.2 mL of water. The solution was stirred for 15 min, as a white precipitate formed. The solid was collected, washed with water, allowed to dry, dissolved in dichloromethane, and heated with activated charcoal. Filtration and solvent evaporation gave 0.50 g (80%) of pale yellow **20**, mp 147–149 °C (lit.[36] mp 146–147 °C). Anal. Calcd: C, 59.1; H, 3.0; N, 31.8. Found: C, 58.9; H, 3.1; N, 31.7. IR (KBr; cm^{-1}) 2135 (str, N=N=N), 1640 (str C=O str). ^1H NMR ($CDCl_3$, 80 MHz; ppm): δ 7.48 (para AA′BB′ q, 8 H, $J = 8.8$ Hz). UV-vis λ_{max} (ϵ, M^{-1} cm^{-1}) 225 nm (23 000).

3,3′-Dinitrobenzophenone (21). This compound was prepared by nitration of benzophenone by the procedure of de Barry and Matthews[47] to yield 22% of **21** with mp 151–153 °C (lit. mp 155 °C[47]).

3,3′-Diaminobenzophenone (22). To a 250-mL round-bottom flask were added 29.1 g (0.129 mol) of stannous chloride dihydrate, 3.5 g (0.129 mol) of **21**, and 75 mL of absolute ethanol. The solution was stirred and heated to 70 °C for 30 min under nitrogen, allowed to cool, poured onto ice, and neutralized with saturated sodium bicarbonate to pH 8. The resulting pale yellow milky solution was extracted with warm ethyl acetate. The organic layer was treated with activated charcoal and dried; the solvent was evaporated to leave a light yellow solid that was recrystallized from aqueous ethanol to give 2.4 g (89%) of **22** as bright yellow fluffy crystals, mp 151.5–152.0 °C (lit.[48] mp 148–149 °C). IR (KBr; cm^{-1}) 3394 and 3287 ($-NH_2$ str), 3182 (wk, C–H str), 1740 (str, C=O). ^1H NMR ($CDCl_3$, 80 MHz; ppm) δ 3.78 (br s, 4 H), 6.81 (m, 2 H), 7.17 (m, 6 H).

3,3′-Diazidobenzophenone (23). To a 35-mL round-bottom flask were added 1.5 g (7 mmol) of **22**, 6 mL of water, and 3.3 mL of concd hydrochloric acid. The mixture was cooled with stirring to 0 °C, and a solution of 1.02 g (15 mmol) of sodium nitrite in 3.6 mL of water was added dropwise. After addition, the reaction mixture was stirred at 0 °C for 1 h; then a solution of 0.92 g of sodium azide in 3.6 mL of water was added, upon which a white precipitate formed. The solid was filtered, rinsed with water, dissolved in dichloromethane, treated with activated charcoal, and dried. The solvent was then removed to leave 1.63 g (87%) of light cream solid **23**, mp 76.5–77.0 °C. Anal. Calcd: C, 59.1; H, 3.1; N, 31.8. Found: C, 58.8; H, 3.0; N, 31.7. IR (KBr; cm^{-1}) 2167 and 2127 (str, N=N=N), 1643 (str, C=O str). ^1H NMR ($CDCl_3$, 80 MHz; ppm) δ 7.28 (m, 2 H), 7.49 (m, 4 H). UV-vis λ_{max} (ϵ, M^{-1} cm^{-1}) 248 nm (51 000).

1,1′-Bis(3-nitrophenyl)ethene (24). Dry triphenylphosphonium bromide (2.63 g, 7 mmol) was stirred in 15 mL of dry tetrahydrofuran placed in a flame-dried 50-mL round-bottom flask and cooled to 0 °C; 1 equiv of *n*-butyllithium (1.55 M in hexane) was added slowly at 0 °C, followed by stirring for 3 h to give a clear, light orange solution of methylene triphenylphosphorane (ylide solution).

Next, a flame-dried 250-mL round-bottom flask equipped with condenser and septum caps was charged with 2.0 g (7 mmol) of compound

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[43] Szmant, H. H.; Deffner, J. F. *J. Am. Chem. Soc.* **1959**, *81*, 958.

[44] Bencze, W. L.; Allen, M. J. *J. Org. Chem.* **1957**, *22*, 352.

[45] Hunsberger, I. M.; Amstutz, E. D. *J. Am. Chem. Soc.* **1949**, *71*, 2635.

[46] Fierz, H. E.; Koechlin, H. *Helv. Chim. Acta* **1918**, *1*, 220.

[47] de Barry, E.; Matthews, M. A. *J. Chem. Soc.* **1924**, 767.

[48] Klemm, L. H.; Mann, R.; Lind, C. D. *J. Org. Chem.* **1958**, *23*, 349.

21 and 60 mL of dry tetrahydrofuran. The resultant solution was cooled to 0 °C under nitrogen, and treated by addition of the ylide solution (see above) in 2-mL portions. The resultant dark brown reaction mixture was then heated under reflux for 18 h, allowed to cool to room temperature, and filtered. The filtrate was diluted with ca. 150 mL of water and extracted with ether. The organic extract was washed with water, 7% aq HCl, water, and brine, then dried over anhydrous sodium sulfate. Filtration and removal of the solvent gave a dark brown solid, which was purified by column chromatography on neutral alumina (Activity II) using hexane/dichloromethane in increasing polarity as the eluent. A near-white solid was collected and recrystallized from methanol to give 1.3 g (65%) of **24**, mp 87–88 °C (lit.[49] mp 88.2–88.9 °C). IR (KBr; cm^{-1}) 925 (str, C=CH_2). ^1H NMR ($CDCl_3$, 80 MHz; ppm) δ 5.73 (s, 2 H), 7.4–8.3 (m, 8 H).

1,1′-Bis(3-aminophenyl)ethene (25). Compound **24** (1.15 g, 4 mmol) was heated at 70 °C with 9.6 g (40 mmol) of stannous chloride dihydrate in 22 mL of absolute ethanol for 30 min under nitrogen. The reaction mixture was allowed to cool and poured over crushed ice. The milky white solution was neutralized with saturated sodium bicarbonate solution to a pH 8–9 and extracted with warm ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to give a white solid that was recrystallized from benzene to give 0.67 g (75%) of **25**, mp 155–156 °C. This material was sufficiently pure for use in the next step. IR (KBr; cm^{-1}) 3394 and 3320 (-NH_2 str), 920 (C=CH_2). ^1H NMR ($CDCl_3$, 80 MHz; ppm (δ 3.62 (br s, 4 H), 6.5–7.2 (m, 8 H).

1,1′-Bis(3-azidophenyl)ethene (26). To 0.5 g (2 mmol) of **25** in a round-bottom flask were added 2 mL of water and 1.1 mL of concd HCl. The solution temperature was lowered to ca. 0 °C, and the diamine diazotized by dropwise addition of a solution of 0.34 g (5 mmol) of sodium nitrate in 1.2 mL of water. The resultant green solution was stirred at 0 °C for 45 min, then treated dropwise with a solution of 0.31 g (5 mmol) of sodium azide in 1.2 mL of water. After addition of the azide solution, the pale yellow reaction mixture was stirred for 10 min, then extracted with dichloromethane. The organic extract was treated with charcoal, dried over anhydrous magnesium sulfate, filtered, and evaporated by a stream of nitrogen to yield a yellow oil that was dried under vacuum. The crude oil solidified in the refrigerator overnight to give 0.46 g (74%) of **26**, mp 33–34 °C. Anal. Calcd: C, 64.1; H, 3.8; N, 32.0. Found: C, 63.1; H, 4.0; N, 31.7. IR (KBr; cm^{-1}) 2115 (str, N=N=N). ^1H NMR ($CDCl_3$, 80 MHz; ppm) δ 5.50 (s, 2 H), 6.9–7.5 (m, 8 H). UV–vis λ_{max} (ϵ, M^{-1} cm^{-1}) 234 nm (34 300).

3,4′-Dinitrostilbene (27). In a 250-mL round-bottom flask was placed 100 mL of freshly distilled benzene (potassium/benzophenone) under nitrogen atmosphere; 5.40 g (25 mmol) of 4-nitrobenzyl bromide and 6.56 g (25 mmol) of triphenylphosphine were added to the flask. The condenser was placed on the flask and refluxed for 1 h under nitrogen atmosphere. The precipitated α-triphenylphosphonio-4-nitrotoluene bromide was collected by filtration and air-dried to give 8.51 g (71%) of white powder.

Next, in a 250-mL round-bottom flask, 2.0 g (13 mmol) of *m*-nitrobenzaldehyde and 6.3 g (13 mmol) of the phosphonium salt were dissolved in 60 mL of methanol under nitrogen. Into the solution was added in small portions 0.7 g (13 mmol) of sodium methoxide over 15 min (solution turns purple), followed by stirring for 1 h at room temperature. The resultant *E*/*Z* mixture of isomers was collected by filtration as a pale yellow precipitate that was air-dried (yield 0.89 g, 25%, mp 176 °C–230 °C).

The *E*/*Z* mixture of 3′,4′-dinitrostilbene (0.89 g, 3.3 mmol) was placed in a 50-mL round-bottom flask with 20 mL of acetone and a crystal of iodine. The mixture was heated at reflux under nitrogen atmosphere overnight. The solution was cooled, and solid (*E*)-3,4′-dinitrostilbene was collected by filtration to give 0.38 g (43%) of bright yellow solid **27**, mp 224–225 °C (lit.[50] mp 207–210 °C, 215 °C[51]).

3,4′-Diaminostilbene (28). In a 50-mL round-bottom flask were placed 14.8 mL of absolute ethanol, 8.34 g (37 mmol) of stannous chloride dihydrate, and 0.96 g (3.6 mol) of **27**. The mixture was heated to 70 °C under nitrogen atmosphere for about 2 h, then cooled to the room temperature. The mixture was poured over ice, and 5% aqueous sodium bicarbonate was added to the mixture until the solution pH was 7–8. The product was extracted with ethyl acetate, and the combined organic extracts were washed with brine solution, treated with charcoal, and dried over anhydrous sodium sulfate. The solvent was evaporated to give 0.46 g (61%) of **28** as a tan solid, mp 149–150 °C, which was sufficiently pure for use in the next step. IR (KBr; cm^{-1}) 3400, 3300, 3200 (overlapping NH_2 str), 965 and 958 (trans CH=CH). ^1H NMR ($CDCl_3$, 80 MHz; ppm): δ 3.7 (br s, 4 H), 6.5–7.5 (complex m, 10 H).

3,4′-Diazidostilbene (29). In a 30-mL round-bottom flask was placed 1.75 mL of H_2O and 0.97 mL of concd hydrochloric acid, followed by 0.46 g (2.2 mmol) of **28**. The flask was cooled in an ice bath and treated dropwise with a solution of 0.32 g (4.6 mmol) of sodium nitrite in 1.1 mL of water. After all the sodium nitrite solution was added, the mixture was stirred for 1 h in the ice bath, passed through filter paper to remove any insoluble material, and placed into the ice bath again. The azide compound was prepared by addition of 0.40 g (6.2 mmol) of sodium azide in 1.1 mL of water was added to the solution dropwise. The mixture foamed immediately and a cream-colored solid precipitated out. The mixture was stirred for 15 min; then the precipitate was collected by the filtration. The solid was dried under the vacuum and redissolved in chloroform. The solution was treated with charcoal and dried with magnesium sulfate. The solvent was evaporated and the product collected lightly yellow solid, yield 0.25 g (57%), mp 89.5–91 °C. Anal. Calcd: C, 64.1; H, 3.8; N, 32.0. Found: C, 63.62; H, 4.00; N, 30.94. IR (KBr; cm^{-1}) 2140 (str, N=N=N), 960 and 955 (trans CH=CH). ^1H NMR ($CDCl_3$, 80 MHz, ppm) δ 6.8–7.6 (m, 10 H). UV–vis λ_{max} (ϵ, M^{-1} cm^{-1}) 329 nm (36 000).

Variable-Temperature Apparatus. Cryogenic ESR spectra were obtained in three ways: (1) in a Suprasil liquid nitrogen dewar (Wilmad Glass) for 77 K fixed temperature measurements; (2) with an APD Cryogenics CS-202 Displex closed-cycle circulated helium cryostat; (3) with an Oxford Instruments ESR9 helium cryostat with DTC-2 temperature controller.

For method 2, the Displex cooling head was attached to a mobile cart holding a vacuum line capable of attaining 5 μTorr. ESR spectral sample holders included an APD Cryogenics commercially available copper rod spindle for solid samples, and a Suprasil optically transparent vacuum tube shroud. We also manufactured a frozen solution matrix sample holder, using a sapphire tube (Saphikon Corp.) with 4.0-mm o.d. 0.9-mm wall thickness, and 28 mm long. The sapphire tube was sealed with either a Viton plug or polytetrafluoroethylene (poly-TFE) tape at one end, and attached with epoxy to a copper base having a machined screw appropriate to fit the Displex lower cooling stage. After placement of a liquid sample in the sapphire sample tube, the open end could be sealed with poly-TFE tape to hold vacuum sufficiently to allow the sample to freeze into a matrix when cooled by the Displex. ESR active impurities in the sapphire tube were in spectral regions that did not interfere with the study of the quintet ESR spectra.

The temperature of the samples in method 2 could be monitored at the base of the Displex cooling stage, using an iron-doped gold–chromel thermocouple. A correction to this nominal temperature was then applied, based upon calibration experiments in which an additional thermocouple was attached to the portion of the sample tube that was to be situated within the ESR sample cavity.

For method 3, temperatures were monitored just below the sample with the gold (0.3% Fe)/chromel sensor of the Oxford Instruments cryostat described above. The temperature readings with sample tubes in place were calibrated prior to each sample use, by measuring the temperatures at the actual position of the sample in the ESR cavity, using an Lake Shore Cryotronics Ga–Al–As calibrated diode sensor (Model XTG-100FP-4D-3).

Diazide Photolyses at 77 K. The appropriate diazide precursor was quickly weighted out into an aluminum-foil-wrapped vial and dissolved in 2-methyltetrahydrofuran, avoiding as much as possible exposure to room light, which tends to turn the diazide reddish. About 500 μL was placed in a quartz 4-mm o.d. ESR tube, frozen, and evacuated to less than 0.05 Torr, and subjected to a 3-fold freeze-thaw purging. The tube was then placed in a transparent Suprasil ESR dewar, frozen with liquid nitrogen, and irradiated through a Pyrex cylindrical filter with a 1000-W xenon arc lamp at a distance of about 10 cm for 1–5 min. The resulting matrix solution (typically yellow or reddish) was placed in the ESR spectrometer cavity with the dewar, and the spectrum recorded at about 9.6 GHz, at 200 μW microwave power intensity.

Curie Analyses of Dinitrenes. A solution of the appropriate diazide precursor in 2-methyltetrahydrofuran was prepared as described in the previous section. For method 2 in the section on variable-temperature apparatus, the solution was carefully syringed into our custom-made sapphire Displex ESR sample tube (see description of Variable-Temperature Apparatus) and sealed off with Teflon tape. The sample tube was attached to the Displex cooling stage, evacuated to <0.1 mTorr, and cooled to 10 K (approximate cooling time 70 min). The sample was irradiated for 1–5 min through a Pyrex tube at a distance of 10 cm using a 1000-W Kratos xenon arc lamp, then warmed to 60–65 K for 15 min. After this annealing step, the sample was recooled to 10 K and maneu-

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(49) Yamada, H.; Tuno, Y.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1459. We thank Prof. Yamada for a reprint of his original synthesis of compound **21**.

(50) Schiemenz, G. P.; Becker, J.; Stoeckigt, J. *Chem. Ber.* **1970**, *103*, 2077.

(51) Harrison, H. A.; Wood, H., Jr. *J. Chem. Soc.* **1926**, 577.

J. Am. Chem. Soc. **1992**, *114*, 9969–9978

vered into the ESR spectral cavity, and data collection was commenced. Once the sample was in place, it was not moved. A plot of signal intensity for a selected peak versus the square root of microwave power was carried out at 10 K, to establish microwave powers at which saturation would not occur. We typically used a ≤500-μW microwave power setting. All spectra were obtained with an identical number of scans and with identical spectrometer power settings. Reproducibility of signal intensities was checked by raising and lowering temperature in the region of 10–50 K, once the annealed sample was produced.

After spectra were obtained, double integration was carried out using standard Bruker software. Plots of double integration intensity versus corrected temperature were analyzed by nonlinear least-squares methods.

For method 3 in the variable-temperature apparatus, the procedure was identical with that described above, save that the samples were frozen and degassed under vacuum in 3-mm o.d. quartz tubes, placed in the cavity of the E-9 ESR spectrometer, cooled to 60–65 K, photolyzed by ca. 1800 pulses from a XeCl excimer laser (Lambda Physik EMG 103 MSC, λ = 308 nm, pulse power at sample ca. 50 mJ), and then examined spectroscopically as described in the previous two paragraphs.

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Photophysics and Photochemistry of 22π and 26π Acetylene–Cumulene Porphyrinoids

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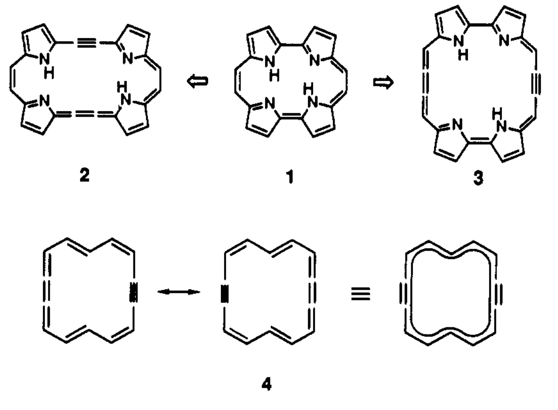
Abstract: The aromatic 26π acetylene–cumulene porphyrinoid **8** has been synthesized by a reaction sequence involving reductive carbonyl coupling of the dialdehyde **12** utilizing low-valent titanium in the crucial step. Like its lower 22π homologs **6** and **7**, the new tetrapyrrolic macrocycle **8** is centrosymmetric in the crystal and has a practically planar ring framework. The photophysical and photochemical properties of **6**–**8** have been studied and compared to those of the related 18π porphycene **5**. The absorption spectrum of **8** has the most red-shifted and intensified visible bands (ϵ_{max} = 119 600 at 889 nm in dichloromethane) of this particular series of (4*n* + 2)π porphyrinoids. None of the compounds exhibit any photoreactivity. The photophysical properties were determined by a combination of techniques, including steady-state thermal lensing, flash photolysis, laser-induced optoacoustic spectroscopy (LIOAS), and steady-state and time-resolved NIR spectroscopy. The 22π and 26π porphyrinoids do not phosphoresce. The triplet energy (E_T) of **7** was therefore measured by way of reversible energy transfer to oxygen yielding singlet molecular oxygen, $O_2(^1\Delta_g)$, indirect detection by LIOAS of the increase in triplet yield induced by $O_2(^3\Sigma_g^-)$-enhanced S → T intersystem crossing afforded the E_T of **6**, and an upper limit of E_T could be obtained by energy-transfer experiments from $O_2(^1\Delta_g)$ to **8**. The quantum yields of fluorescence, triplet formation, and the E_T values dropped significantly on going from **5** to **6**–**8** (all measurements at room temperature). The triplet energies of **6**, **7**, and **8** are all below the energy of $O_2(^1\Delta_g)$. Compound **7**, with the highest E_T of the three, produces $O_2(^1\Delta_g)$ with a quantum yield of Φ_Δ = 0.06 through a reversible energy-transfer mechanism. Although this value is about six times smaller than Φ_Δ of **5**, the phototherapeutic activities of both **5** and **7** toward tumors in mice are comparable. The Φ_Δ values for **6** and **8** are lower than 10^{-3}; hence, these porphyrinoids do not function as photodynamic sensitizers.

Introduction

Porphycene (**1**; Scheme I), isomeric to porphyrin from which it is derived formally by a mere reshuffling of the pyrrole and methine moieties, is a novel tetrapyrrolic macrocycle commanding interest from many points of view.[1] Numerous investigations[2] of **1** bear out the anticipated close relationship of this molecule to porphyrin, but they also reveal noticeable differences between the two isomers, qualifying **1** as a porphyrinoid in its own right.

The finding that porphycenes and metalloporphycenes are porphyrin-like pigments—and thus promise practical applications in various domains—was an incentive to us to devise expanded porphycenes expected to match or complement the expanded porphyrins[3] and related macrocycles[4] in their physical and chemical properties. In order to be endowed with aromatic stability, the new porphyrinoids envisioned must contain main conjugation pathways involving (4*n* + 2) π electrons with *n* > 4.[5]

Scheme I. Expansion of Porphycene (**1**) by Acetylene–Cumulene Structural Units to **2** and **3** and Juxtaposition of These Homologs with 1,2,8,9-Tetradehydro[14]annulene (**4**)



A clue as to how porphycenes might be translated into variants with an expanded structure meeting the electronic prerequisites is provided by the bonding in the intriguing acetylene–cumulene [4*n* + 2]dehydroannulenes.[6] As exemplified by the prototypical

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