J. Am. Chem. Soc. 1994, 116, 8784–8792

Models for Intramolecular Exchange in Organic π-Conjugated Open-Shell Systems: 3-Nitrenophenyl and 4-Nitrenophenyl Units Connected by 2,5-Furandiyl, 2,5-Thiophenediyl, and 2,5-Pyrrolediyl Nonalternant Exchange Linkers

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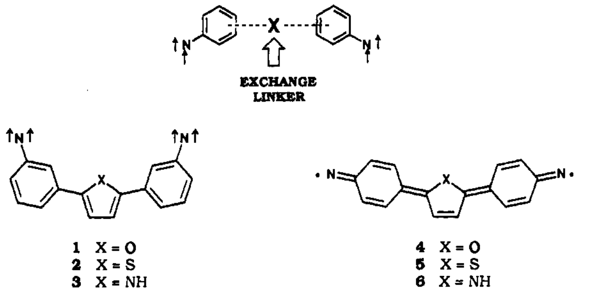
Received May 12, 1994[⊗]

Abstract: The first bis(arylnitrenes) linked by heterocyclic pseudoaromatic rings were generated in a glassy, 77 K 2-methyltetrahydrofuran matrix by photolysis at wavelengths >300 nm: 2,5-bis(3-nitrenophenyl)furan (**1**); 2,5-bis(3-nitrenophenyl)thiophene (**2**); 2,5-bis(3-nitrenophenyl)pyrrole (**3**); 2,5-bis(4-nitrenophenyl)furan (**4**); 2,5-bis(4-nitrenophenyl)thiophene (**5**); 2,5-bis(4-nitrenophenyl)pyrrole (**6**). Systems **1–3** gave quintet ESR spectra with $|D/hc| \approx 0.16\ \mathrm{cm^{-1}}$ having thermal peak intensity variations consistent with each system being a pseudodisjoint ground state singlet dinitrene and a thermally populated excited quintet state, similar to behavior exhibited by structurally related bis(arylnitrenes) (Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547). On the basis of Curie law ESR spectral peak intensity behavior, multiple conformations of **1** and **3** were deduced as having different values of ΔE(singlet→quintet): for **1**, we found peaks with ΔE = 60 and 100 cal/mol; for **3**, we found peaks with ΔE = 18 and 110 cal/mol. The major quintet peak of **2** has thermal behavior consistent with ΔE = 88 cal/mol. Systems **4–6** gave triplet biradical ESR spectra consistent with quinonoidal biradical structures having zero field splitting values of $|D/hc| = 0.137\ \mathrm{cm^{-1}}$ ($|E/hc| = 0.016\ \mathrm{cm^{-1}}$), $|D/hc| = 0.190\ \mathrm{cm^{-1}}$ ($|E/hc| = 0.006\ \mathrm{cm^{-1}}$), and $|D/hc| = 0.183\ \mathrm{cm^{-1}}$ ($|E/hc| = 0.012\ \mathrm{cm^{-1}}$), respectively. The biradical ESR spectral intensities for **4–6** decrease with decreasing temperature, showing these to be ground state singlet biradicals.

Introduction

We have previously described computational[1-3] and experimental work[4,5] aimed at a systematic study of intramolecular exchange coupling as a function of molecular structure in conjugated open-shell molecules. While other groups have studied bis(nitroxides)[6-8] and polycarbenes, much of our experimental work on small molecule intramolecular exchange coupling has focused upon bis(arylnitrene) systems. Bis(arylnitrenes) offer considerable advantages of conformational certainty about the nitrene nitrogen, ease of generation, and an increasing body of electron spin resonance (ESR) spectroscopic data allowing identification of different spin states that may be observed.[9] In this contribution, we describe the first[10] study of open-shell molecules that employ heterocyclic nonalternant π-systems of 2,5-connectivity as linkers -X- (Scheme 1) in organic open-shell model systems. The linkers 2,5-furandiyl, 2,5-thiophenediyl, and 2,5-pyrrolediyl were used to couple both 3-nitrenophenyl and 4-nitrenophenyl groups to yield dinitrenes **1–6**.

Scheme 1



Synthesis

Figure 1 outlines the syntheses of diazide precursors **7–12** to the dinitrenes **1–6**. The diazides were synthesized via acid-catalyzed cyclocondensation of the appropriate dinitro-1,4-dibenzoylethane with polyphosphoric acid, Lawesson's reagent,[11] or ammonia, followed by reduction with stannous chloride in ethanol and then diazotization/azidification by standard procedures. All the product diazides are stable in the absence of direct light and may be kept for months in a refrigerator.

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1994.

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

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

(4) Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1991**, *4*, 459.

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(6) (a) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952. (b) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238. (c) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847. (d) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180.

(7) (a) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 125. (b) Itoh, K.; Takui, T.; Teki, Y.; Kinoshita, T. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 49. (c) Furukawa, K.; Matsumura, T.; Teki, Y.; Kinoshita, T.; Takui, T.; Itoh, K. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 251. Cf. also the references in these works.

(8) (a) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744. (b) Dougherty, D. A.; Jacobs, S. J.; Silverman, S. K.; Murray, M. M.; Shultz, D. A.; West, A. P., Jr.; Clites, J. A. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 289.

(9) Lahti, P. M. In *Research Trends*; Menon, J., Ed.; Council of Scientific Research Integration: Trivandrum, India, 1992; Vol. 3; pp 179–192.

(10) For a class of diradicaloid singlet state molecules based upon 3,4-disubstituted furans, thiophenes, and pyrroles, cf. the following. (a) Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088. (b) Zilm, K. W.; Merrill, R. A.; Grenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567. (d) Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3671. (d) Bush, L. C.; Heath, R. B.; Berson, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 9830. For the case described in (d), a triplet state may be observed under some circumstances of photolysis.

(11) Shridhar, D. R.; Jogibhukta, M.; Shanthan Rao, P.; Handa, V. K. *Synthesis* **1982**, 1061.

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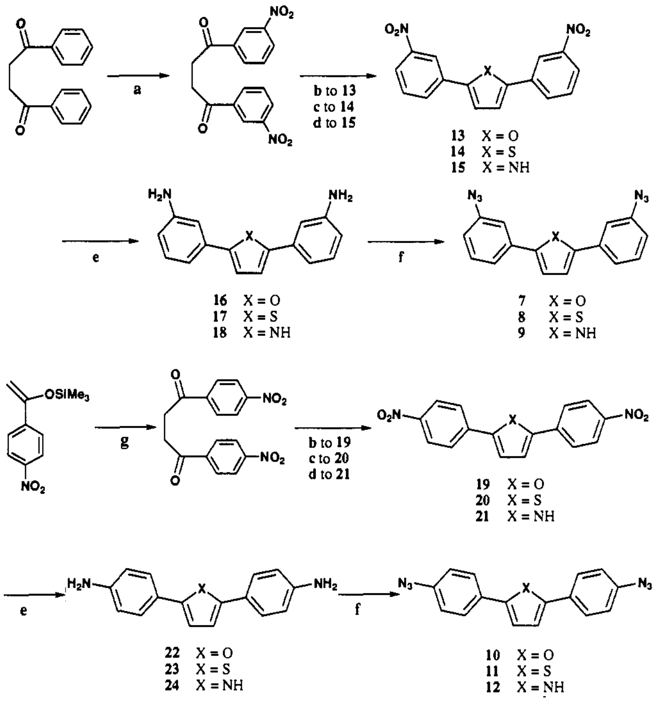

Figure 1. Synthesis of diazide precursors. Conditions: (a) fuming HNO_3/ –40 °C; (b) polyphosphoric acid, 140–145 °C; (c) $(ArP(=S)S-)_2$; (d) $NH_4OAc/HOAc/\Delta$; (e) $SnCl_2 \cdot 2H_2O/EtOH/\Delta$; (f) aqueous HCl/ $NaNO_2$/0 °C, then NaN_3; (g) $PhIO/BF_3 \cdot OEt_2$, –60 to –45 °C.

Results

Dissolution of the appropriate diazides **7–12** in degassed 2-methyltetrahydrofuran, freezing to 77 K or below, and photolysis with a 1000 W xenon arc lamp (Pyrex or Oriel 300–400 nm band pass filter or 320 nm setting on a monochromator) for 2–5 min yields the X-band ESR spectra shown in Figures 2 and 3. These spectra disappear upon thawing of the matrix (>95 K) but are stable at 77 K or below. The 77 K solutions from photolyses of diazides **7–9** tend to be greenish but can show some darker coloration upon extended photolysis: thawing the sample quenches the color and leaves a straw yellow solution. The 77 K photolyzed matrix solutions from diazides **10–12** turn from reddish to extremely deep blue upon brief warming to approximately the melting point of the 2-methyltetrahydrofuran. This blue color fades within seconds to a straw yellow color as the matrix melts to a free-flowing liquid. Brief warming of a 77 K photolyzed sample of **12** to give the blue color, followed by swift refreezing in liquid nitrogen, showed that the ESR spectrum in Figure 3 had disappeared except for a radical peak at $g \approx 2$, although the blue color persisted at 77 K.

Discussion

Pseudodisjoint Dinitrenes 1–3. Photolysis at 77 K of **7** gives radical impurity ESR peaks at ca. 3380 G, a mononitrene H_{xy} peak at 6970 G ($|D/hc| = 1.008\ cm^{-1}$)[12] due to cleavage of only one diazide moiety, and a series of peaks at 500, 1780 (br), 2515, 2710, 3060, 6500, and 8600 (wk) G, which we attribute to the quintet state of **1**. Photolysis at 77 K of **8** gives a mononitrene H_{xy} peak at 6960 G ($|D/hc| = 1.005\ cm^{-1}$) and peaks at 405, 890, 1260, 1630, 2500, 2840, 4700, 5750, 6420, and 8620 (very weak) G attributed to quintet **2**. Photolysis at 77 K of **9** gives a mononitrene H_{xy} peak at 6930 G ($|D/hc| = 0.993\ cm^{-1}$) and peaks at 460, 1580, 2540, 2750, 2970, 4500, 6400, and 8590 (very weak) G attributed to quintet **3**.

The zero field splitting (zfs) of the mononitrenes is typical for arylnitrenes without extended conjugation[12] and is reasonable for systems **1–3** with *meta* connectivity of their nitrene moieties. The quintet peaks are similar in position and appearance to those of disjoint bis(arylnitrenes) (**25–28**, Scheme 2) studied by ourselves[5,13] and the Iwamura group.[6,14,15] If the two highest field peaks are taken to be quintet H_1 and H_2 transitions in each case for Figure 2, we can estimate[16] zfs values of $|D/hc| = 0.163$ cm^{-1} and $|E/hc| = 0.009\ cm^{-1}$ for both **1** and **2**, while $|D/hc| =$ $0.161\ cm^{-1}$ and $|E/hc| = 0.008\ cm^{-1}$ for **3**. Although **1–3** are not alternant systems, our earlier computations[3] indicate that the heteroatoms in these systems have little if any participation in the spin delocalization of **1**. As a result, **1–3** may be considered as connectivity analogues of Iwamura's disjoint system **28**.[14,15] The ESR spectral similarity of quintets **1–3** to disjoint dinitrenes **27** and **28** supports this analogy.

The most recent AM1-CI and PM3-CI computational work by us[17] finds that the various states of **1–3** are degenerate to within <50 cal/mol, consistent with their disjoint natures. In variable temperature ESR studies, the quintet spectra exhibit nonlinear intensity behavior with reciprocal temperature, showing that the quintets are thermally excited states. The low to modest microwave power settings (<500 μW) used by us for these studies were chosen to minimize the signal saturation effects that can confound interpretation of a Curie law plot[18] and have proven[13–15] to be appropriate for a varient of bis(arylnitrenes). For a system made up of a pair of triplets weakly coupled by antiferromagnetic (AFM, Scheme 3) exchange, a state energy ordering of singlet < triplet < quintet is expected[19] with $\Delta E(\text{singlet}\rightarrow\text{triplet}) = 2J$ and $\Delta E(\text{singlet}\rightarrow\text{quintet}) = 6J$. Equation 1 is appropriate for this model and has been used elsewhere for open-shell systems[5,13–15,19] that are adequately described by the weakly interacting triplet model. The spectral intensity I obeys eq 1, where J is the exchange coupling constant, R is the Boltzman constant, T is absolute temperature, and C is an arbitrary constant chosen to fit the observed spectral intensities.

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

We carried out nonlinear least squares fits to eq 1 of the ESR intensities I of the major intensity peaks for **1–3** versus reciprocal

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[12] $|D/hc|$ estimated by the method set forth by Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

[13] Lahti, P. M.; Ling, C.; Yoshioka, N.; Rossitto, F. C.; van Willigen, H. *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 17.

[14] Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33.

[15] Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

[16] $|D/hc|$ estimated by the method used in Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. The assignment of zero field splitting parameters by this method is not unambiguous, due to uncertainties of interpreting the spectra of randomly oriented quintet spectra with large zfs.

[17] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221. An OPEN-(4,4) C.I.=(5,1) MECI keyword set was used to compute the states of **1–3**, while OPEN(2,2) C.I.=(5,2) was used for **4–6**. All computations were done using MOPAC 6.0 (Stewart, J. J. P. QCPE Program 455 (1989)), by the general procedures of ref 3, modified as described in this footnote.

[18] Strictly speaking, the observation of a linear Curie-type variation of spectral intensity as a function of reciprocal absolute temperature is dependent upon the assumption that rapid equilibrium between ground and thermally excited states of different multiplicity is maintained (see ref 10d above and 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). Presumably this criterion is readily met in dinitrenes, since the spin–orbit coupling moments of their heteroatoms should enhance intersystem crossing rates. More pernicious is the fact that linear Curie law behavior may be observed for systems with extremely small (degenerate) energy gaps between ground and excited states, as well as for systems with quite substantial gaps. Inherent limitations of interpreting Curie-type experiments with ESR spectroscopy are described by Berson J. A. In *The Chemistry of the Quinonoid Compounds*: Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1988; p 462 ff. Some cases of ground state multiplicity deduction by Curie analysis, in which Hund's rule as interpreted for molecules is apparently violated, are discussed in Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

[19] Itoh, K. In *Magnetic Molecular Materials, NATO ASI Series*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 67 ff.

[20] Doi, T.; Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 8928.

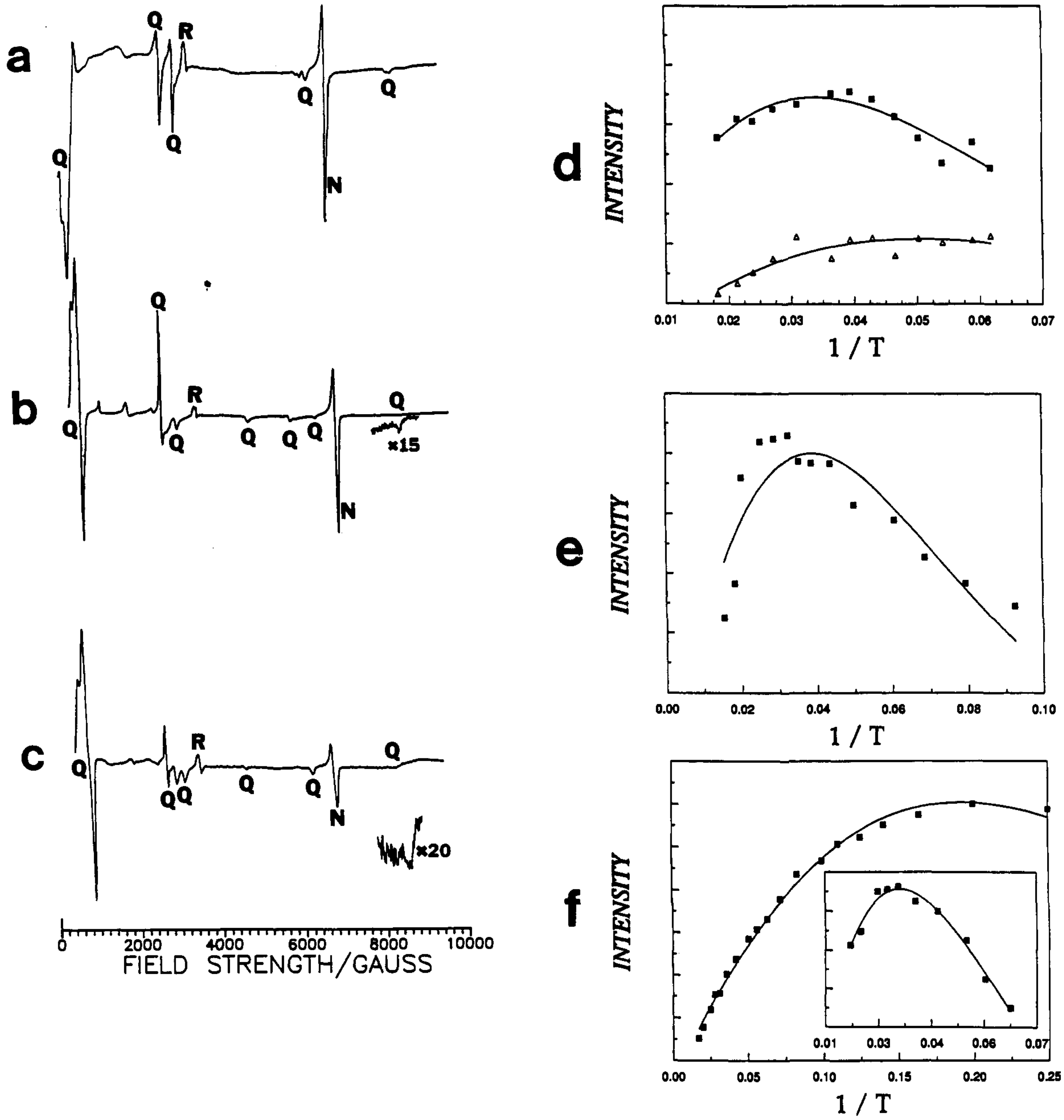


Figure 2. ESR spectra from photolysis of diazides **7** (curve a), **8** (curve b), and **9** (curve c) at 77 K in 2-MeTHF, $\nu_0 = 9.58$ GHz. Q = quintet dinitrene, R = radical impurity, N = mononitrene triplet peaks. Plot d has Curie intensity data for the 2515 G (▲) and 2710 G (■) peaks of **1**, plot e has Curie data for the 2500 G peak of **2**, plot f has Curie data for the 2540 G (main plot) and 2750 G (inset, ordinate expanded 30-fold relative to main plot) peaks of **3**.

temperature $1/T$, using the program PS-Plot (Polysoft, Salt Lake City, UT) with C and J as adjustable parameters. The statistical uncertainties given below for J are the 95% univariant confidence limits. The fitted plots to the data are shown in the insets of Figure 2. Using this procedure, $J = 16.7 \pm 0.1$, 14.6 ± 2.1, and 3.0 ± 0.2 cal/mol, yielding ΔE(singlet→quintet) = 100, 88, and 18 cal/mol for the major ESR peaks of **1**–**3**, respectively.

If all peaks present are assumed to be due to quintets, we find evidence that the multiple peaks in such dinitrene spectra are not necessarily due to a single, geometrically well-defined bis(arylnitrene). The weak peak at 2515 G from photolysis of **7** displays a different temperature dependence from that of the more intense 2710 G peak and has an intensity variation consistent with $J = 10.1 \pm 2.5$ cal/mol, ΔE(singlet→quintet) $\approx$ 60 cal/mol by the method used above. We attribute the different behaviors of thes peaks to the presence of different conformational isomers (see Scheme 4) of quintet **1**.

In a similar manner, the ESR spectrum from photolysis of diazide **9** shows impressive thermal variations over the range of 4–77 K. The major peak at 2540 G shows intensity variation consistent with a quintet state that is nearly degenerate with other states of lower energy and remains fairly intense even at 4–10 K. However, the peaks at 460, 2750, and 2970 G all disappear at temperatures below 15 K, indicating that these are not due to the same ESR spectral carrier giving the 2540 G peak. Finally, a set of peaks at 850, 1400–1740, 2150–2250, and 5650 G increases in intensity at lower temperatures, but at a rate rather faster than does the peak at 2540 G; these peaks are very weak at >60 K, although the peaks at 2540, 2750, and 2970 G are visible. All of these effects are reversible if temperature is cycled between 4 and 60 K. These effects are illustrated by the series of spectra taken at 60, 22, and 5 K and shown in Figure 4. The results are consistent with up to three different species.

We believe that the peak at 2540 G is caused by one conformer of quintet bis(arylnitrene) **3**, while those at 2750 and 2970 G are caused by another quintet conformer, which has a different value of J from the first conformer.[21] The peaks at 2750 and 2970 G are only moderately strong and so are somewhat problematic to

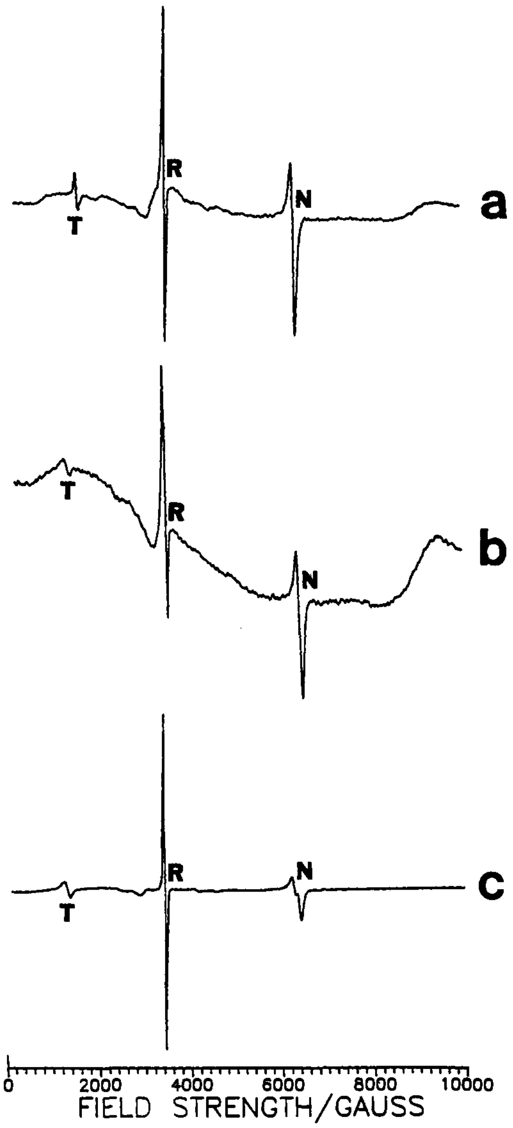
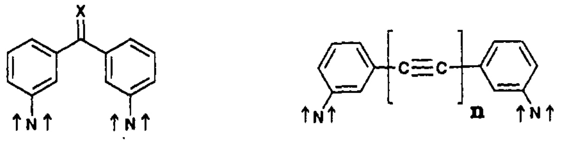


Figure 3. ESR spectra from photolysis of diazides **10** (curve a), **11** (curve b), and **12** (curve c) at 77 K in 2-MeTHF, ν_0 = 9.58 GHz. T = triplet biradical, R = radical impurity, N = mononitrene triplet peaks.

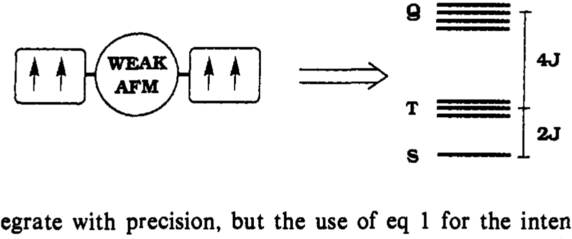
Scheme 2



25 X = CH_2
26 X = O

27 n = 1
28 n = 2

Scheme 3



integrate with precision, but the use of eq 1 for the intensity variation of the 2750 G peak was fit to J = 18.0 ± 0.8 cal/mol, corresponding to ΔE(singlet→quintet) ≈ 110 cal/mol. This second conformation of **3** thus has an exchange coupling strength fairly similar to that of the major conformations studied in **1**–**2**.

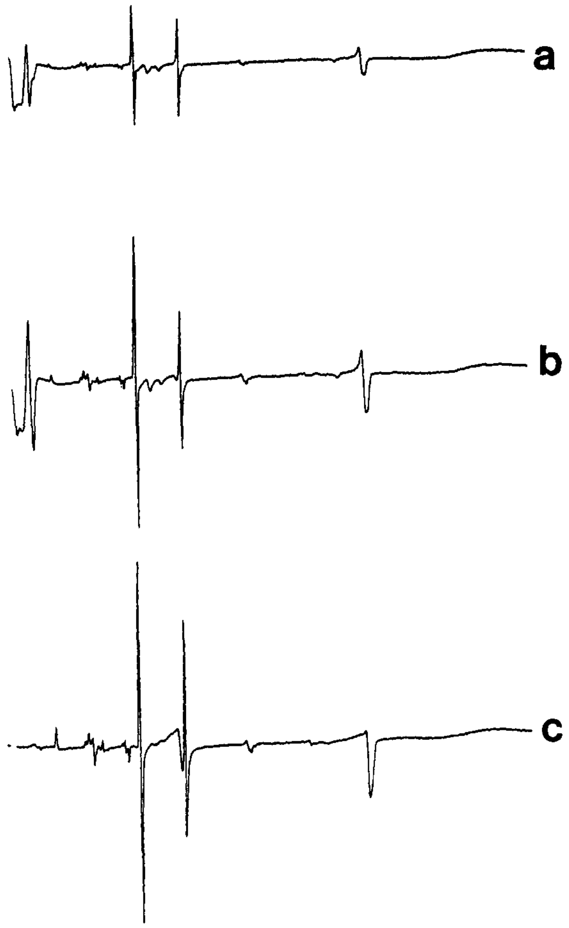
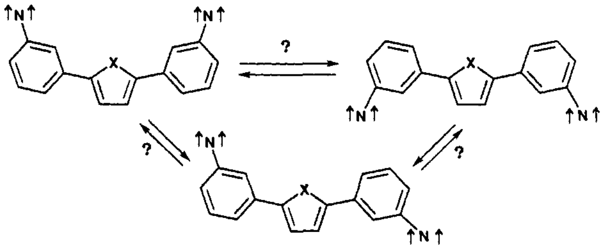


Figure 4. ESR spectra at different temperatures from photolysis of a single sample of **9** in 2-MeTHF. ν_0 = 9.34 GHz, 100–9800 G. Temperatures: (a) 60 K, (b) 22 K, (c) 5 K. The same ordinate scale is used for curves a–c, so the relative peak intensities are properly displayed.

Scheme 4



The general appearance of the quintet ESR spectra is presumably a reflection of the relative proportions of different conformations produced in the photolyses of structural analogues **7**–**9**. The spectra from the photolyses of **8**–**9** are very similar, suggesting that the conformational mix of bis(arylnitrenes) **2** and **3** is similar in our experiments; if so, the conformational distribution in **1** produced from **7** must be somewhat different, since our samples of **1** have a weak peak in the 2500 G region and a strong peak in the 2700 G region, while the situation is the reverse for **2** and **3**. Our results show that, in weakly coupled systems, conformational difference can have an observable effect upon the magnitude of exchange coupling. By correlating ESR spectral peak positions and thermal behavior for conformationally fixed model compounds, we hope that it may eventually prove

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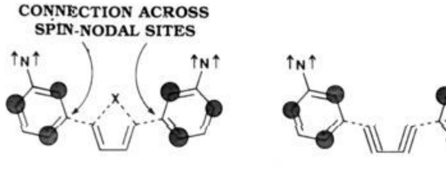
(21) An example of conformational effects upon energetic spacing between states of different multiplicity for 3,3′-benzophenonedinitrene has previously been described in Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Kaise, M. *Chem. Lett.* **1993**, 837. Differing electronic behavior as a function of conformation has been also noted for dicarbenes in ref 7 and diradicals in Rajca, A.; Utamapanya, S.; Smithhisler, D. J. *J. Org. Chem.* **1993**, *58*, 5650.

Scheme 5



1-3
PSEUDODISJOINT

28
DISJOINT

possible to assign peaks in specific regions of randomly oriented ESR quintet spectra to particular conformations.

The complexity of these spectra lead one to query about possible assignments to the triplet excited states of these dinitrenes, which should be thermally populated if the model of eq 1 for weakly coupled triplets is applicable here. Simulation of the spectra of dicarbenes and dinitrenes in randomly oriented phases presents substantial problems due to their large zfs. We could not confidently assign any of the observed peaks to triplet dinitrene species. This problem has been encountered in other dinitrene work, where triplet spectral features were not identified for disjoint species.[5,6a] In one case of a disilane-linked dinitrene, assignment of a peak at 2430 G was interpreted as consistent[20] with the model of eq 1, and the suggestion has been made[15] that peaks in the 2400 G region are consistent with one of the triplet dinitrene ESR transitions. The assignment in the disilane case was supported by the thermal variation of the peak intensity, which followed that expected for the Itoh[7a] model. Some peaks in our spectra may be interpretable as being triplet dinitrenes on the basis of such arguments, and the presence of such peaks is expected on the basis of the Itoh model unless they are too broad and weak to be observed in the presence of the quintet spectra. But, the thermal intensity variation of the peaks in our spectra does not fit well to models where some peaks are due to triplets and others are due to quintets. As a result, we feel that the complexity of interpreting quintet ESR spectral transitions in randomly oriented environments for these molecules renders triplet dinitrene assignments uncertain without further, considerable theoretical and experimental analysis.

Aside from the fairly modest electronic perturbations caused by conformational isomerism and different heteroatoms in the central heterocyclic ring, **1**–**3** all behave as antiferromagnetically coupled bis(nitrene) systems, consistent with our computational description[3] that **1**–**3** are pseudodisjoint. Scheme 5 illustrates a connectivity-based comparison of **1**–**3** to Murata and Iwamura's disjoint system **28**. The central rings in **1**–**3** connect two phenylnitrene units across sites of very small spin density (orbital nodes).[3] Connectivity across nodal (inactive) sites is typical for many systems that are disjoint in the Borden/Davidson sense.[22] System **28** is properly disjoint in this sense, while nonalternant **1**–**3** also behave in a disjoint manner, because the heteratom connections do not change **1**–**3** from acting like **28** in their exchange behavior. As a result, both the disjoint and pseudodisjoint systems have singlet ground states with low-lying quintet states and similar ESR spectra. Overall, although the nonalternant heterocyclic central rings in **1**–**3** are structurally novel, electronically they give exchange coupling that leads to disjoint dinitrene behavior similar to that seen other systems.

Quinonoidal Dinitrenes 4–6. Photolysis of **10** gives radical impurity ESR peaks, a mononitrene H_{xy} peak at 6160 G ($|D/hc|$ = 0.717 cm^{-1}), and small peaks at 1490, 1960, 2340, 2860, 3810, 4360, and 4860 G. Photolysis of **11** gives a mononitrene peak at 6240 G ($|D/hc|$ = 0.744 cm^{-1}) and weak peaks at 1270, ~2260 (br), 4200, and 4430 G. Photolysis of **12** gives a mononitrene peak at 6240 G ($|D/hc|$ = 0.744 cm^{-1}) and weak peaks at 1300, ~2280 (br), 4080, and 4510 G. The small zfs of the mononitrene byproducts in all these *para*-substituted cases indicates considerable conjugation[12] between the nitrene π-spin density and the heterocyclic rings. Assuming that both nitrene sites in the dinitrene will have similarly good conjugation with the central heterocyclic rings, we expect dinitrenes **3**–**4** to be conjugated, quinonoidal biradicals.

The weak peaks from photolyses of **10**–**12**, shown in expanded format in Figure 5 (with the radical impurity peaks at $g \approx 2$ omitted for clarity), are consistent with the triplet biradical ESR spectra expected for **4**–**6**. The triplet features in these spectra could be simulated using the method of Kottis and Lefebvre,[22] as is also shown in Figure 5. The spectrum of **4** was fit to g_{xx} = 2.000, g_{yy} = 2.003, g_{zz} = 1.995, with zfs parameters $|D/hc|$ = 0.137 cm^{-1} and $|E/hc|$ = 0.016 cm^{-1}. The spectrum of **5** is a reasonable fit to g_{xx} (=g_{zz}) = 2.001 and g_{yy} = 2.004, with $|D/hc|$ = 0.190 cm^{-1} and $|E/hc|$ = 0.006 cm^{-1}, although the parallel turning points were too weak to be observed in the experimental spectrum. The spectrum of **6** is a reasonable fit to g_{xx} (=g_{zz}) = 2.001 and g_{yy} = 2.004, and $|D/hc|$ = 0.183 cm^{-1} and $|E/hc|$ = 0.012 cm^{-1}, again with the experimental parallel turning points too weak and/or broad to be observed. Some variation in these fitting parameters is possible, while still giving good fits to the observed spectra, but we could not achieve reasonable simulated fits without use of anisotropic g tensors.

The spectra are quite similar to those of other quinonoidal dinitrenes studied by us, which have large zfs despite long distances between their localized nitrene σ-electrons: one difference is the substantial size of $|E/hc|$ in **4**–**6**. Previously studied quinonoidal dinitrenes such as **29** and **30** in Scheme 6 are more geometrically cylindrical than **4**–**6** and so have small or zero $|E/hc|$ values.[23–28] The spectral intensities of **4**–**6** all reversibly decrease as the temperature is lowered below 77 K, confirming that these peaks are due to thermally populated excited states. This behavior is similar to that shown by related dinitrenes **29** and **30**.[24]

Computational Structures for 1–6. Whereas benzenoid-type structures are found for **1**–**3** by the quintet AM1-CI computations that were mentioned above, triplet AM1-CI computations show quinonoidal structures[26] to be preferred for **4**–**6**. The two sets of computed structures are shown in Figure 6, along with selected bonding parameters. For systems **4**–**6**, AM1-CI predicts singlet biradical ground states with low-lying triplet states ≲100 cal/mol higher in energy.[17] The near-degeneracy of states in **4**–**6** is reasonable, since the exchange coupling between the two localized, unpaired electrons on the nitrene nitrogens must be small. By valence bond arguments elsewhere discussed,[19] one would expect the singlet to be favored by a small amount in such a weakly interacting situation. Since neither of these electrons is actually part of the delocalized π-orbital cloud, exchange apparently takes place via spin polarization of the π-cloud by the large σ-spin densities of the unpaired electrons, giving rise to zfs $|D/hc|$ values that are substantially larger than expected if a simple through-space dipolar mechanism were the sole contributor to zfs. In this situation, the small polarized π-spin density on the nitrene nitrogen would interact strongly with the large, localized σ-spin density on the same nitrogen, giving a large one-center contribution to the total zfs. We have previously described how this effect would qualitatively increase the zfs expected for localized quinonoidal biradical dinitrenes.[24]

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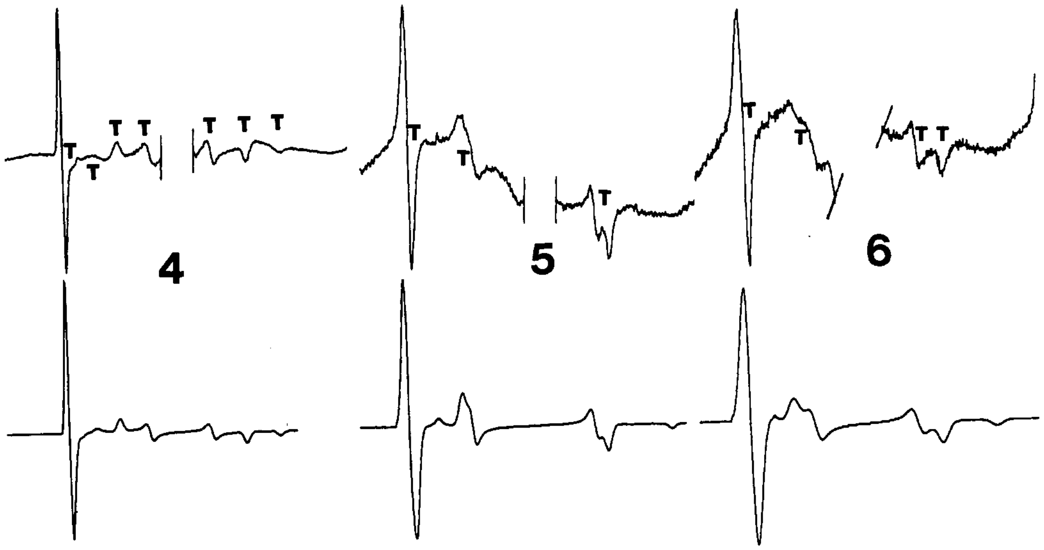
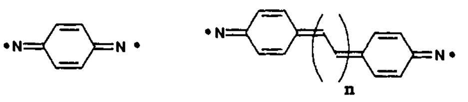


Figure 5. Expanded ESR spectra of dinitrenes **4**–**6** (radical peaks at $g \approx 2$ were deleted for clarity, curves a–c respectively), ν_0 = 9.58 GHz. Range = 500–6000 G for all experimental spectra. Biradical peaks are marked with T. Triplet biradical simulation curves are shown below each experimental spectrum, using the procedure described in the text.

Scheme 6



29 **30**

Summary

The use of nonalternant conjugated systems as structural linking groups can extend considerably the scope of structures which may be used in the study of intramolecular exchange between electrons. Connection across the 2,5-positions of furan, thiophene, and pyrrole leads to pseudodisjoint coupling for *meta,meta'* connection of two phenylnitrene units, resulting in near-degeneracy of singlet ground states and experimentally observable quintet excited states. Connection across the same positions leads to localized, quinonoidal biradical systems for *para,para'* connection of two phenylnitrene units, in accord with arguments advanced previously by us.[3] Zwitterionic resonance effects in some heteroatomic nonalternant systems may perturb the energetic ordering of states that are closely spaced due to pure connectivity-based agruments. As a result of the large number of possibilities that are available with nonalternant structure moieties that are not available only with alternant units, we anticipate that nonalternant ring systems will be increasingly of interest in the study of open-shell molecules.

Experimental Section

General. Starting reagents were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrophotometer and were calibrated by reference against a polystyrene standard. ^{1}H-NMR spectra were recorded on an IBM Instruments NR-80A FT-NMR and were referenced against internal tetramethylsilane on the δ scale in parts per million. UV–vis spectra were recorded on a Shimadzu UV-260 double beam recording spectrophotometer. All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory. High-resolution electron impact mass spectra were obtained at the Midwest Center for Mass Spectrometry, with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262). Tetrahydrofuran, pyridine, and pentane were purified by distillation from potassium/benzophenone, barium oxide, and calcium hydride, respectively.

1,4-Diphenyl-1,4-butanedione. Dibenzoylethene (6.62 g, 28.0 mmol) was mixed with 177 mL of 2-propanol, 1.8 mL of concentrated hydrochloric acid, and 180 mg of 5% Pd/C and shaken at an initial hydrogen pressure of 50 psi for 30 min. The solution was heated to boiling and filtered and then left to crystallize. The yellowish-white needles were then recrystallized from ethanol to yield 4.44 g (66.5%) of product with mp 144–145 °C (lit.[29] mp 147–148 °C): ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.46 (s, 4H), 7.3–7.6 (m, 6 H), 7.9–8.2 (m, 4 H); IR (KBr disk; cm^{-1}) 1680 (C=O).

1,4-Bis(3-nitrophenyl)-1,4-butanedione. Fuming nitric acid (115 mL) was cooled to –40 °C (acetonitrile/dry ice) and 5 g (21.0 mmol) of 1,4-diphenyl-1,4-butanedione was added with mechanical stirring while maintaining the temperature at –40 °C. After the addition was complete the mixture was stirred for a further 40 min at –40 °C and then the temperature was raised to 0 °C. The solution was then poured onto 1000 g of ice with stirring. After the ice melted, the solution was filtered and a white solid was isolated. The solid was washed with water and allowed to dry and then recrystallized from benzene to yield 2.81 g (41%) of very pale yellow crystals of product with mp 159–161 °C (lit.[30] 155–157 °C): ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.55 (s, 4H), 7.71 (t, 2 H), 8.2–8.6 (m, 4 H), 8.86 (s, 2 H); IR (KBr; cm^{-1}) 3080, 3055 (C=*C*—*H*), 2925 (C—*C*—*H*), 1695 (C=O), 1535 (NO_2), 1355 (NO_2).

2,5-Bis(3-nitrophenyl)furan (13). 1,4-Bis(3-nitrophenyl)-1,4-butanedione (2 g, 6.09 mmol) and 10 g of polyphosphoric acid were heated at 140–145 °C for 90 min and then immediately rinsed onto ice with water. The solid was collected and washed repeatedly with water and dried. One recrystallization from glacial acetic acid (charcoal) gave 1.39 g (74%) of product **13** with mp 190–193 °C: ^{1}H NMR (80 MHz, DMSO-d_6) δ 7.45 (s, 2 H), 7.76 (pseudo t, J = 8.0 Hz, 2 H), 8.1–8.4 (m, 4 H), 8.60 (pseudo t, J = 1.6 Hz, 2 H). Anal. Calcd for $C_{16}H_{10}N_2O_5$: C, 61.94; H, 3.25; N, 9.02. Found: C, 61.95; H, 3.35; N, 9.00.

2,5-Bis(3-aminophenyl)furan (16). **13** (1.5 g, 4.83 mmol), 10.89 g (48.3 mmol) of stannous chloride dihydrate, and 50 mL of ethanol were heated under N_2 at reflux for 60 min. The solution was allowed to cool, poured into ice–water, and neutralized with 2 M sodium hydroxide solution until a pH of ca. 8 was reached. The aqueous solution was extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed with brine and dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to yield 1.22 g of solid **16**, which was recrystallized from benzene to give 0.88 g (73%) of pale fluffy needles, mp 201–203 °C dec: ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.7 (br s, 4 H), 6.5–6.7 (m, 2 H), 6.68 (s, 2 H), 7.0–7.3 (m, 6 H); IR (KBr; cm^{-1}) 3425, 3325 (NH_2). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.73; H, 5.54; N, 11.13.

2,5-Bis(3-azidophenyl)furan (6). In a 25 mL beaker, 0.704 g (2.81 mmol) of **16** was stirred with a solution of 2.9 mL of water and 1.6 mL of concentrated hydrochloric acid. The white paste was cooled to 0 °C and a solution of 0.408 g (5.91 mmol) of sodium nitrite in 1.5 mL of water was added dropwise to give a thick orange paste. The paste was allowed to sit for 15 min at 0 °C and then a solution of 0.384 g (5.91 mmol) of sodium azide in 1.5 mL of water was added dropwise. The solution was

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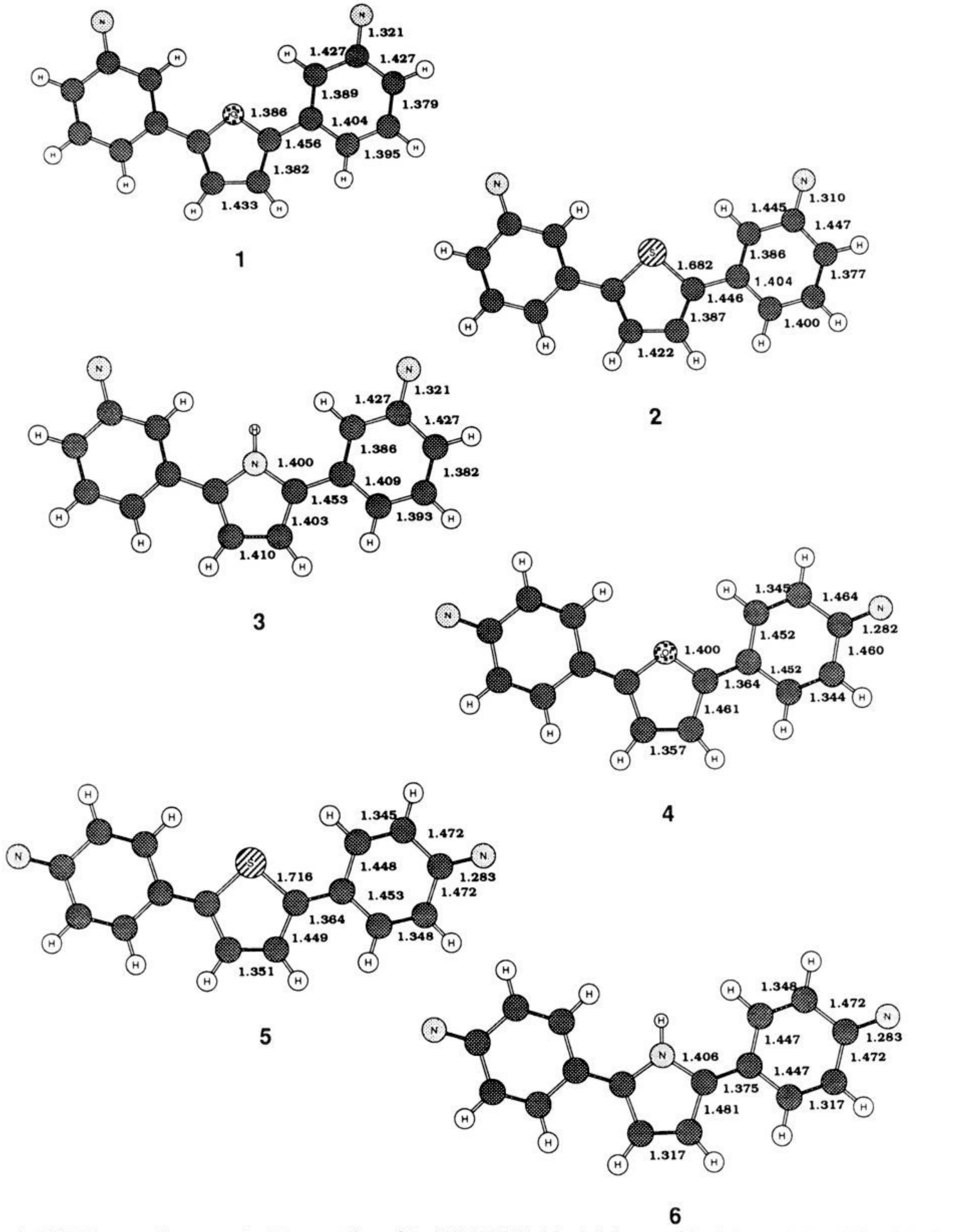

Figure 6. AM1-CI computed structures for dinitrenes **1**–**3** at a C.I.=(5,1) OPEN(4,4) level of theory, and for dinitrenes **4**–**6** at a MS=1 C.I.=(5,2) OPEN(2,2) level of theory. Selected bond lengths are given in angstroms, bond angles in degrees. See also ref 28.

stirred intermittently for 1 h and then the pale greyish precipitate was collected and washed with water and ice-cold ethanol. The solid was then dissolved in dichloromethane, boiled with charcoal for a few minutes, and filtered. The solvent was dried over anhydrous sodium sulfate and the solvent removed in vacuo to yield a pale cream solid; yield 0.73 g (86%). The solid was recrystallized from pentane and then ethanol (charcoal); yield 0.35 g (41%) of **5** with mp 111.5–112.5 °C: ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.76 (s, 2 H), 6.8–7.1 (m, 2 H), 7.1–7.6 (m, 6 H); IR (KBr; cm^{-1}) 2125 (N_3); UV–vis (THF, λ_{max}/nm, ϵ/L mol^{-1} cm^{-1}) 333 (35 600). Anal. Calcd for $C_{16}H_{10}N_6O$: C, 63.58; H, 3.33; N, 27.79. Found: C, 63.45; H, 3.38; N, 27.98.

2,5-Bis(3-nitrophenyl)thiophene (14). A mixture of 3 g (9.14 mmol) of 1,4-bis(3-nitrophenyl)-1,4-butanedione and 4.44 g (10.98 mmol) of Lawesson's[11] reagent were heated under reflux in 50 mL of toluene for 45 min. The solution was allowed to cool to room temperature and then chilled in ice. The solid was isolated and dissolved in dichloromethane/acetone and then chromatographed on silica gel using 80:20 dichloromethane:hexane as the eluent. Evaporation of the solvent and recrystallization from glacial acetic acid gave 2.47 g (99%) of bright yellow solid **14**, mp 180–180.5 °C: ^{1}H NMR (80 MHz, DMSO-d_6) δ 7.81 (dd, *J* = 8.9 Hz, *J'* = 8.8 Hz, 2 H), 7.85 (s, 2 H), 8.1–8.3 (m, 4 H), 8.46 (pseudo t, *J* = 1.8 Hz, 2 H); IR (KBr; cm^{-1}) 1620, 1525, 1355 (NO_2). Anal. Calcd for $C_{16}H_{10}N_2O_4S$: C, 58.89; H, 3.09; N, 8.58. Found: C, 58.65; H, 3.38; N, 8.34.

2,5-Bis(3-aminophenyl)thiophene (17). A mixture of 1.5 g (4.60 mmol) of **14**, 10.35 g (46.0 mmol) of stannous chloride dihydrate, and 50 mL of ethanol was heated under nitrogen at reflux for 40 min. The solution was allowed to cool and poured into ice–water and then neutralized with 2 M sodium hydroxide solution until a pH of ca. 8 was reached. The aqueous solution was extracted with 3 × 100 mL of ethyl acetate. The combined extracts were washed with brine and dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to yield 1.27 g of a pale cream solid. The solid was recrystallized from chloroform (charcoal) to give 0.79 g (65%) of fluffy cream-colored crystals of **17**, mp 183–185 °C: ^{1}H NMR (80 MHz, DMSO-d_6) δ 3.3 (br s, NH_2 protons), 6.4–6.6 (m 2 H), 6.7–7.2 (m, 6 H), 7.30 (s, 2 H); IR (KBr; cm^{-1}) 3390, 3290 (NH_2). Anal. Calcd for $C_{16}H_{14}N_2S$: C, 72.15; H, 5.30; N, 10.51. Found: C, 72.22; H, 5.32; N, 10.53.

2,5-Bis(3-azidophenyl)thiophene (7). To 0.479 g (1.80 mmol) of **17** was added a chilled mixture of 2 mL of distilled water and 1.1 mL of concentrated hydrochloric acid. The hydrochloride salt was cooled to <0 °C and a solution of 0.261 g (3.78 mmol) of sodium nitrite in 0.92 mL of distilled water was added dropwise over a few minutes to give a clear orange-red solution. This was stirred at 0 °C for 45 min, whereupon a yellow precipitate was apparent. A solution of 0.246 g (3.78 mmol) of sodium azide in 0.92 mL of distilled water was added dropwise and the solution stirred for a further 20 min. The solid was collected, washed with water, and taken up in dichloromethane. The organic solution was dried over anhydrous magnesium sulfate and filtered and then boiled with charcoal and filtered again. Evaporation of the solvent left 0.5 g (87%) of a shiny pearl solid, which when recrystallized from ethanol gave 0.42 g (74%) of **7**, mp 140.5–141.0 °C: ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.9–7.1 (complex m, 2 H), 7.2–7.5 (m, 6 H), 7.29 (s, 2 H); IR (KBr; cm^{-1}) 2115, 2145 (N_3); UV-vis (THF, λ_{max}/nm, ε/L mol^{-1} cm^{-1}) 335 (33 800). Anal. Calcd for $C_{16}H_{10}N_6S$: C, 60.37; H, 3.17; N, 26.39. Found: C, 60.44; H, 3.28; N, 26.67.

2,5-Bis(3-nitrophenyl)pyrrole (15). A mixture of 2 g (6.09 mmol) of 1,4-bis(3-nitrophenyl)-1,4-butanedione, 2.33 g (30.23 mmol) of ammonium acetate, and 25 mL of glacial acetic acid was refluxed for 21 h. The mixture was allowed to cool and then poured into ice–water. The solid was collected and washed repeatedly with water, sucked dry, and immediately recrystallized from glacial acetic acid to afford 1.64 g (87%) of orange fluffy crystals of **15**, mp 265–266 °C: ^{1}H NMR (80 MHz, DMSO-d_6) δ 6.95 (d, *J* = 2.4 Hz, 2 H), 7.67 (pseudo t, *J* = 8.0 Hz, 2 H), 8.0–8.4 (m, 4 H), 8.69 (pseudo t, *J* = 1.8 Hz, 2 H), 9.8 (br s, 1 H); IR (KBr; cm^{-1}) 3390 (NH), 1620, 1525, 1355 (NO_2). Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.58. Found: C, 62.29; H, 3.73; N, 13.59.

2,5-Bis(3-aminophenyl)pyrrole (18). **15**, (2 g, 6.5 mmol), 0.5 g of 5% Pd–C, and 180 mL of ethanol were shaken for 19 h under 44 psi of hydrogen. The mixture was filtered and the solvent evaporated. The solid was recrystallized from toluene to yield 1.11 g (69%) of white solid **18**, mp 203–204 °C dec: ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.7 (br s, 4 H), 6.50 (d, *J* = 2.6 Hz, 2 H), 6.6–7.3 (m, 8 H), 8.5 (br s, 1 H); IR (KBr; cm^{-1}) 3420, 3350, 3195 (NH), 1610, 1590, 1495. Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.09; H, 6.06; N, 16.85. Found: C, 77.24; H, 6.12; N, 16.73.

2,5-Bis(3-azidophenyl)pyrrole (9). To 1 g (4.0 mmol) of **18** was added a chilled mixture of 4.1 mL of distilled water and 2.2 mL of concentrated hydrochloric acid to give a white paste of the dihydrochloride salt. The paste was cooled to −10 °C and a solution of 0.581 g (8.42 mmol) of sodium nitrite in 2.1 mL of distilled water was added dropwise over a few minutes. The dark brown paste was stirred for 1 h at <0 °C. A solution of 0.548 g (8.42 mmol) of sodium azide in 2.1 mL of distilled water was added dropwise to produce a grey, metallic precipitate. The solid was collected and dissolved in dichloromethane. The organic extract was washed with saturated sodium bicarbonate solution and brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was boiled with charcoal and filtered again. Evaporation of the solvent left 0.83 g (69%) of a brown solid. Column chromatography on silica gel using 50:50 dichloromethane:hexane as eluent gave 0.38 g (31%) of pale shiny cream-colored crystals of **9**, mp 121–123 °C: ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.60 (d, 2 H, *J* = 2.6 Hz), 6.8–7.0 (m, 2 H), 7.2–7.4 (m, 6 H), 8.5 (br s, 1 H); IR (KBr; cm^{-1}) 3450 (NH), 2115 (N_3), 1608, 1588; UV-vis (THF, λ_{max}/nm, ε/L mol^{-1} cm^{-1}) 341 (35 400). Anal. Calcd for $C_{16}H_{11}N_7$: C, 63.79; H, 3.68; N, 32.53. Found: C, 63.69; H, 3.75; N, 32.33.

4-Nitroacetophenone Trimethylsilyl Enol Ether. A three-necked round-bottom flask equipped with a condenser and 250 mL addition funnel was flame-dried under nitrogen. The flask was charged with 50 mL of dry tetrahydrofuran and 23.5 g (0.146 mol) of hexamethyldisilazane and cooled to −50 °C. The hexamethyldisilamide base was generated by addition via a syringe of 58 mL (0.146 mol) of a 2.5 M solution of *n*-butyllithium in hexanes. The basic solution was stirred for 20 min during which time the addition funnel was filled with a solution of 20 g (0.121 mol) of 4-nitroacetophenone in 300 mL of dry tetrahydrofuran. After the 20 min had elapsed the solution was added dropwise at a bath temperature of −60 to −80 °C over 60 min. The dark brown solution was stirred at −75 °C for 30 min; then 20 mL (17.1 g, 0.158 mol) of distilled chlorotrimethylsilane was added over a 10 min period. The solution became clearer and lighter in color. The bath temperature was allowed to warm to 10 °C and then the bath was removed and the light brown solution heated at reflux for 13 h. A white solid separated. The solution was allowed to cool and diluted with 300 mL of pentane and filtered. The filtrate was diluted again with 400 mL of pentane and then filtered though Celite. The volume was reduced to ca. 500 mL and the clear brown solution filtered again and dried over anhydrous magnesium sulfate. The solvent was evaporated to give 33.0 g of a brown liquid which was distilled under vacuum to give 22.4 g (78%) of clear pale yellow liquid product:[31] ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 4.56 (d, 1 H, *J* = 2.3 Hz), 5.02 (d, 1 H, *J* = 2.3 Hz), 8.2–7.5 (AA'BB' quartet, 8 H, *J* = 9.1 Hz).

1,4-Bis(4-nitrophenyl)-1,4-butanedione. An oven dried 1 L, three-necked round-bottom flask was equipped with a condenser, a septum cap, and a stopper. The flask was flame-dried under nitrogen and charged with 11.22 g (51 mmol) of iodosobenzene (CAUTION: may explode if heated dry to the melting point!) and 450 mL of dry dichloromethane (distilled from P_4O_{10}). To this suspension was added 18.8 mL (21.71 g, 153 mmol) of boron trifluoride etherate to produce a yellow solution. Not all of the solid dissolved. The solution was cooled to −55 °C and 22.3 g (94 mmol) of 4-nitroacetophenone trimethylsilyl enol ether was added over a 10 min period. Addition of the enol caused a pale cream coloration. The reaction mixture was stirred for 1 h at −60 to −45 °C and then left to reach room temperature overnight. The dark brown solution was washed with saturated sodium bicarbonate and brine and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give a reddish slush. This was rinsed from the flask and triturated with ice-cold ether to give 6.23 g of a sandy yellow powder. The aqueous washings were extracted once with dichloromethane. The organic extract was washed with brine and dried over anhydrous magnesum sulfate. The solvent was evaporated in vacuo to yield 3.31 g of a pale sandy yellow powder. The combined powders were recrystallized from chloroform to yield 7.29 g of brown crystals. Reduction of the mother liquor afforded an additional 1.77 g of a pale yellow powder, mp 194–196 °C. The brown crystals were again recrystallized from chloroform (charcoal) to yield another 6.77 g of the pale yellow powder, mp 195–196 °C (lit.[31] mp 195–197 °C); overall yield was 8.54 g (55%): ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.52 (s, 4 H), 8.1–8.45 (AA'BB' quartet, *J* = 8.8 Hz); IR (KBr, cm^{-1}) 1690 (C=O), 1528 (NO_2), 1350 (NO_2).

2,5-Bis(4-nitrophenyl)furan (19). The procedure here was identical to that used for 2,5-bis(3-nitrophenyl)furan, using 3 g (9.1 mmol) of 1,4-bis(4-nitrophenyl)-1,4-butanedione as reactant. **19**: yield 1.51 g (80%); mp 272–273 °C dec; lit.[32] mp 210 °C dec; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.03 (s, 2 H), 7.8–8.4 (AA'BB' quartet, 8 H); IR (KBr; cm^{-1}) 1515 (NO_2), 1345 (NO_2).

2,5-Bis(4-aminophenyl)furan (22). The same procedure described for 2,5-bis(3-aminophenyl)furan was used, with 1.5 g (4.8 mmol) of **19** as reactant. The resultant orange solid was recrystallized from benzene (charcoal) to yield 0.74 g (61%) of **22** with mp 213–216 °C: ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.7 (br s, 4 H), 6.52 (s, 2 H), 6.4–7.7 (AA'BB' quartet, 8 H, *J* = 8.4 Hz); IR (KBr; cm^{-1}) 3445, 3360 (NH_2), 1625. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 77.02; H, 5.71; N, 11.04.

2,5-Bis(4-azidophenyl)furan (10). The same procedure described for the synthesis of **7** was followed, using 0.66 g (2.64 mmol) of **22** as a reactant. The product solid was recrystallized from ethanol to give 0.40 g (50%) of pale orange crystals of **10** with mp 138–139 °C: ^{1}H NMR

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(80 MHz, $CDCl_3$) δ 6.68 (s, 2 H), 6.9–7.8 (AA'BB' quartet, $J = 8.8$ Hz, 8 H); IR (KBr; cm^{-1}) 2100, 2135 (N_3); UV–vis (THF, λ_{max}/nm, ϵ/L mol^{-1} cm^{-1}) 349 (shoulder, 25 500), 354 (48 200). Anal. Calcd for $C_{16}H_{10}N_6O$: C, 63.58; H, 3.33; N, 27.79. Found: C, 63.43; H, 3.38; N, 25.63.

2,5-Bis(4-nitrophenyl)thiophene (20). A similar procedure as outlined for 2,5-bis(3-nitrophenyl)thiophene was followed, using 2.3 g (7.1 mmol) of 1,4-bis(4-nitrophenyl)-1,4-butanedione and 3.4 g (8.5 mmol) of Lawesson's[11] reagent. Workup and recrystallization from glacial acetic acid gave 1.69 g (73%) of bright orange solid **20**, mp 257–258 °C: MS *m/z* calcd for $C_{16}H_{10}N_2O_4S$ ($M^{+\bullet}$) 326.0361, found 326.0365; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.51 (s, 2 H), 7.6–8.4 (AA'BB' quartet, 8 H, J = 8.9 Hz); IR (KBr; cm^{-1}) 1515 (NO_2), 1345 (NO_2).

2,5-Bis(4-aminophenyl)thiophene (23). A mixture of 1.5 g (4.6 mmol) of **20**, 10.37 g (46 mmol) of stannous chloride dihydrate, and 100 mL of ethanol was heated at 70 °C under nitrogen for 5 h. The reaction mixture was allowed to cool and poured into ice–water. The mixture was neutralized with saturated sodium bicarbonate solution until a pH of ca. 8–9 was reached and then extracted with ethyl acetate. The organic extract was washed with water and brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo to yield 0.91 g (74%) of **23** as a brown-bronze powder which could be recrystallized from toluene to give mp 168–169 °C. This compound was used as soon as possible in the next step: ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.70 (br s, 4 H), 6.5–7.5 (AA'BB' quartet, 8 H, J = 8.6 Hz), 7.07 (s, 2H); IR (KBr; cm^{-1}) 3420, 3340, 3210 (NH_2), 1620, 1510.

2,5-Bis(4-azidophenyl)thiophene (11). A procedure similar to that outlined for **10**, using 0.95 g (3.6 mmol) of **23**, yielded 1.0 g (88%) of pale orange crystals of **11**. Recrystallization from ethanol gave an analytically pure sample, mp >360 °C dec: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.23 (s, 2 H), 6.9–7.7 (AA'BB' quartet, $J = 8.7$ Hz, 8 H); IR (KBr; cm^{-1}) 2095, 2135 (N_3); UV–vis (THF, λ_{max}/nm, ϵ/L mol^{-1} cm^{-1}) 353 (37 900). Anal. Calcd for $C_{16}H_{10}N_6S$: C, 60.37; H, 3.17; N, 26.39. Found: C, 60.24; H, 3.04; N, 26.09.

2,5-Bis(4-nitrophenyl)pyrrole (21). A similar procedure to that outlined for 2,5-bis(3-nitrophenyl)pyrrole was followed, using 2 g (6.1 mmol) of 1,4-bis(4-nitrophenyl)-1,4-butanedione and 2.3 g (30.2 mmol) of ammonium acetate. Workup and recrystallization from acetic anhydride gave 1.72 g (92%) of maroon solid **21**, mp 283–286 °C: MS *m/z* calcd for $C_{16}H_{11}N_3O_4$ ($M^{+\bullet}$) 309.0749, found 309.0747; ^{1}H NMR (80 MHz, DMSO-d_6) δ 7.03 (singlet in damp solvent, 2 H), 8.0–8.4 (AA'BB' quartet, 8 H, J = 9.1 Hz); IR (KBr; cm^{-1}) 3410 (NH), 1515 (NO_2), 1345 (NO_2).

2,5-Bis(4-aminophenyl)pyrrole (24). The same procedure as that outlined for **18** was followed, using 1.5 g (4.85 mmol) of **21**, to give a quantitative yield of a brown solid. Recrystallization from benzene gave 0.95 g (79%) of orange crystals of **24**, mp 200–201 °C. This was used as soon as possible in the next step: ^{1}H NMR (80, MHz $CDCl_3$) δ 3.55 (br s, 4 H), 6.37 (d, J = 2.6 Hz, 2 H), 6.6–7.4 (AA'BB' quartet, 8 H, J = 8.6 Hz), 8.3 (br s, 1 H); IR (KBr; cm^{-1}) 3345 (NH), 1620, 1505, 1285.

2,5-Bis(4-azidophenyl)pyrrole (12). A procedure similar to that outlined for **9**, using 0.42 g (1.69 mmol) of **24**, gave 0.15 g (29%) of **12** as a shiny cream solid, mp >360 °C dec: MS *m/z* calcd for $C_{16}H_{11}N_7$ ($M^{+\bullet}$) 301.1076, found 301.1075; ^{1}H NMR ($CDCl_3$) δ 6.54 (d, 2 H, 2.5 Hz), 6.9–7.6 (AA'BB' quartet, 8 H, J = 8.5 Hz), 8.4 (br s, 1 H); IR (KBr; cm^{-1}) 3440 (NH), 2140, 2100 (N_3); UV–vis (THF, λ_{max}/nm, ϵ/L mol^{-1} cm^{-1}) 358 (25 100).

Electron Spin Resonance Experiments. The appropriate precursor diazide (1–2 mg) was dissolved in 2.5 mL of 2-methyltetrahydrofuran, freshly distilled from potassium permanganate under argon. Then 300 μL of this solution was placed in a 4 mm o.d. quartz ESR tube, subjected to a 3-fold freeze–thaw cycle, and sealed under vacuum. ESR spectra were obtained using a Bruker ESP-300 multiscan X-band spectrometer at 9.57 GHz, 100 kHz field modulation frequency, 5.2 G modulation amplitude, and <500 μW microwave power. Control experiments of ESR signal intensity versus the square root of microwave power showed that signal saturation of putative dinitrene resonances did not occur under cryogenic temperature conditions at these settings. Spectral line positions were calibrated vs a solid diphenylpicrylhydrazyl standard (g = 2.0037).

ESR measurements at 77 K were carried out in frozen 2-methyltetrahydrofuran solutions with liquid nitrogen in a Suprasil finger dewar. Matrix solutions were photolyzed at 77 K for 2–5 min with a 1000 W xenon arc lamp from a distance of 10 cm through either a Pyrex or an Oriel no. 51810 filter to screen out light of <300 nm. Variable temperature ESR measurements for photolyses of the diazides (except for **9**) were carried out in the ESP-300 spectrometer cavity equipped with an Air Products LT-3-110 Helitran helium cryostat. A sample was photolyzed in a quartz dewar in liquid nitrogen at 77 K and then transferred as swiftly as possible (<1 s) directly into the cavity cryostat, which had been precooled to ≤50 K. Temperatures at the sample position were monitored using an iron-doped gold–chromel thermocouple (Scientific Instruments, Inc. Model CG07FC-4). ESR peak intensities were obtained as a function of temperature under identical scanning and microwave power conditions and then doubly integrated using standard Bruker ESP-300 software with the same integration endpoints for all spectra of a given sample that were obtained at various temperatures. Spectra were obtained during each run while temperatures were raised and lowered (without going above 60 K) to establish reproducibility and to establish that no effect of sample annealing occurred during variable temperature measurements.

Variable temperature ESR measurements for photolysis of **9** were carried out in the ESP-300 spectrometer cavity equipped with an Oxford Instruments ESR 900 helium cryostat. Temperature calibration of the cryostat was carried out using carbon glass electrodes. Photolysis and insertion into the cavity of the sample was carried out as described above for **4–5**, as was spectral acquisition and double-integration.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (PRF 25968-AC4). Support from the National Science Foundation (CHE 9204695) is also gratefully acknowledged.