Catenation of Heterocyclic Non-Kekulé Biradicals to Tetraradical Prototypes of Conductive or Magnetic Polymers

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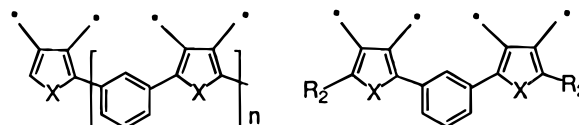
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Abstract: Methods are described for the synthesis of bis-diazene precursors of catenated tetraradicals. Photodeazetation in a low-temperature matrix of the *N*-tosylpyrrole member of the series (**13**) gives mainly the monodeazetated biradical **34**, which is characterized by its ESR spectrum as a triplet species. Determination of the absolute number of spins present and analysis of the kinetics of the photolysis show that the tetraradical **12** is present to the extent of only 0.2−0.5% of the concentration of the biradical. The spectrum of the tetraradical **12** therefore cannot be observed under these conditions, and its spin remains unknown. Photodeazetation of the bis-diazene precursor (**35**) in the thiophene series gives successively the green monodeazetated biradical **36** and the (also green) bis-deazetated tetraradical **11**. The reactions of compound **11** with alkenes in thawed matrices and its lack of an ESR spectrum characterize the species as a singlet. The tetraradical **11** is a prototype of a nonclassical polymeric conductor. Because of the presence of "half-filled" NBMOs, the frontier electrons of such molecules may be exceptionally conductive.

Accompanying[1] and previous[2] papers show how variation of the group X can be used to control the spacings of the multiplet energies of a series of heterocyclic non-Kekulé molecules **1**−**3**. These species are formed in thermal or photochemical deazetations of their corresponding diazenes **4**−**6**. That work

1: X = O　　　**4:** X = O

2: X = S　　　**5:** X = S

3: X = NR　　**6:** X = NR
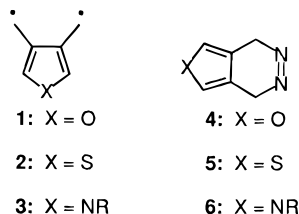
demonstrates singlet ground states for the furan and thiophene biradicals **1** and **2** as well as for the pyrrole biradicals **3** with electron-releasing or moderately electron-withdrawing N-substituents (R). Both singlet and triplet species can be observed when the R group is strongly electron-withdrawing, as in R = *p*-toluenesulfonyl (Ts) or *p*-bromobenzenesulfonyl (Bs).

Such non-Kekulé biradical units might serve as building blocks for the eventual construction of multiradical "nonclassical"[3] polymers with useful and theoretically significant properties. Specifically, in π-electron theory, the monomeric units **1**−**3** each contain a pair of half-filled nearly degenerate, nominally nonbonding molecular orbitals (NBMOs). The triplet monomers[1b,2d] might lead to conductively insulating high-spin polymers, such as **9**, with ferromagnetic properties.[4] On the

n is large

7: X = O　　　　　　**10:** X = O, R₂ = H

8: X = S　　　　　　**11:** X = S, R₂ = CH₃

9: X = NTs　　　　　**12:** X = NTs, R₂ = H

other hand, from singlet monomers such as **1** and **2**,[1a,2a−c,e] catenation should lead to antiferromagnetic low-spin polymers **7** and **8**, for example, in which half-filled electron bands derived from these NBMOs would confer the capability for metallic

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(1) (a) Bush, L. C.; Heath, R. B.; Feng, X. W.; Wang, P. A.; Maksimovic, L.; Song, A. I.; Chung, W. C.; Berinstain, A. B.; Scaiano, J. C.; Berson, J. A. *J. Am. Chem. Soc.* **1996**, *118,* 1406 (accompanying paper) and references cited therein. (b) Bush, L. C.; Maksimovic, L.; Feng, X. W.; Lu, H. S. M.; Berson, J. A. *Ibid.* **1996**, *118,* 1416 (accompanying paper) and references cited therein.

(2) (a) Berson, J. A. *Pure Appl. Chem.* **1987**, *59,* 1571. (b) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111,* 3659. (c) Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *Ibid.* **1989**, *111,* 3671. (d) Bush, L. C.; Heath, R. B.; Berson, J. A. *Ibid.* **1993**, *115,* 9830. (e) Heath, R. B.; Bush, L. C.; Feng, X. W.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.* **1993**, *97,* 13355. (f) Scaiano, J. C.; Wintgens, V.; Bedell, A.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110,* 4050. (g) Scaiano, J. C.; Wintgens, V.; Haider, K.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111,* 8732.

(3) (a) Tyutyulkov, N.; Kanev, I.; Polansky, O.; Fabian, J. *Theor. Chim. Acta* **1977**, *46,* 191. (b) Tyutyulkov, N.; Schuster, P.; Polansky, O. *Theor. Chim. Acta* **1983**, *63,* 291. (c) Tyutyulkov, N.; Polansky, O. E.; Schuster, P.; Karabunarliev, S.; Ivanov, C. I. *Theor. Chim. Acta* **1985**, *67,* 211. (d) Tyutyulkov, N.; Karabunarliev, S. C. *Int. J. Quantum Chem.* **1986**, *29,* 1325. (e) Tyutyulkov, N.; Polansky, O. E. *Chem. Phys. Lett.* **1987**, *139,* 281. (f) Tyutyulkov, N.; Ivanov, C. I.; Schopov, I. *Int. J. Quantum Chem.* **1988**, *34,* 361. (g) Tyutyulkov, N.; Karabunarliev, S.; Ivanov, C. *Mol. Cryst. Liq. Cryst.* **1989**, *176,* 139.

(4) See *inter alia*: (a) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. J. *Am. Chem. Soc.* **1967**, *89,* 5076. (b) Itoh, K. *Chem. Phys. Lett.* **1967**, *1,* 235. (c) Mataga, N. *Theor. Chim. Acta* **1968**, *10,* 372. (d) Yoshizawa, K.; Hoffmann, R. *Chem. Eur. J.* **1995**, *1,* 403 and references cited therein. (e) Kollmar, C.; Kahn, O. *Acc. Chem. Res.* **1993**, *26,* 259. (f) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24,* 88. (g) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26,* 179. (h) Buchachenko, A. L. *Russ. Chem. Rev.* **1990**, *59,* 307. (i) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21,* 114. (j) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88,* 201. (k) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33,* 385. (l) Rajca, A. *Chem. Rev.* **1994**, *94,* 871. (m) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31,* 180. (n) Kanno, F.; Inoue, K.; Kago, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115,* 847. (o) Fang, S.; Lee, M.-S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1995**, *117,* 6727. (p) West, A. P., Jr.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118,* 1452. (q) Kearley, M. L.; Ichimura, A. S.; Lahti, P. M. *J. Am. Chem. Soc.* **1995**, *118,* 5235. (r) Dannenberg, J. J.; Liotard, D.; Halvick, P.; Rayez, J. C. *J. Phys. Chem.* **1996**, *100,* 9631. (s) Okada, K.; Imakura, T. Oda, M.; Murai, H.; Baumgarten, M. *J. Am. Chem. Soc.*, in press.

conduction[5] without doping. Thus, in the present work,[1,6] the tunability of a common structural motif might find eventual application in practical devices and also in the search for understanding of the spin interactions among very weakly bound electrons in extended π-conjugated systems.

Connectivity in Multiradicals. To preserve a non-Kekulé structure with its NBMO-rich spectrum of energy levels, and to prevent the formation of new π-bonds in both the high-spin and low-spin series, the catenation of the biradicals must avoid connectivity patterns that locate odd electrons at adjacent sites. More generally, it is useful to be able to predict at least the minimum number of Hückel π-NBMOs from a given connectivity. In the case of alternant hydrocarbons, this has been possible traditionally from the Coulson−Rushbrooke−Longuet−Higgins theorem: when the compound is written in the structure with the maximum number of bonds, the number of such NBMOs (in the case of non-Kekulé hydrocarbons) is equal to or (in the case of 4*m* cyclopolyenes, *m* = 1, 2 ...) greater than the number of π-framework carbon atoms that bear odd electrons.[7] For tetramethyleneethane, for example, the number of NBMOs is 2, and for cyclobutadiene, it is at least zero (actually 2). Strictly, this rule cannot be applied to heterocyclic or nonalternant monomers such as **1**−**3** or to polymers derived by their catenation. Recently, however, a generalized form of the theorem has been proposed by Tyutyulkov and co-workers[3] to cover such cases, which are designated as "quasi-alternants". In quasi-alternant systems, every Hückel graph of N atoms is characterized by a maximum subset T consisting of N_t noncontiguous homonuclear π-centers. The π-centers not belonging to T may be heteronuclear. If for a given Hückel system $2N_t > N$ is fulfilled, then its energy spectrum displays at least ($2N_t - N$) NBMOs. In the cases of **1**−**3**, for example, $N = 7$, $N_t = 4$, and the numbers of NBMOs ≥ 1 (actually 2).

Also, in the high-spin systems, the linkages must be made through coupling elements that favor ferromagnetic interactions between the component triplet monomer units. Although the theoretical basis for such choices is still in a state of development,[4c,d,f,l−r] we have chosen the *m*-phenylene coupler, which has a history in biradical chemistry dating back to the studies of Schlenk and Brauns in 1915[8a] and continuing to the present.[4,8b]

To explore the electron spin properties of substances which can serve as building blocks for the multiradical polymers **7**−**9**, we describe here the development of synthetic methods for the catenation of diazene precursors **4**−**6**, the application of these methods to the synthesis of the bis-diazene precursors of the set of tetraradicals **10**−**12**, and the nature of the species generated by deazetation of the bis-diazenes.

Synthesis of Catenated Bis-Diazene Precursors. Scheme 1 shows the general route we have previously used[1,2] for the

Scheme 1

4: X = O

5: X = S

6: X = NR

13
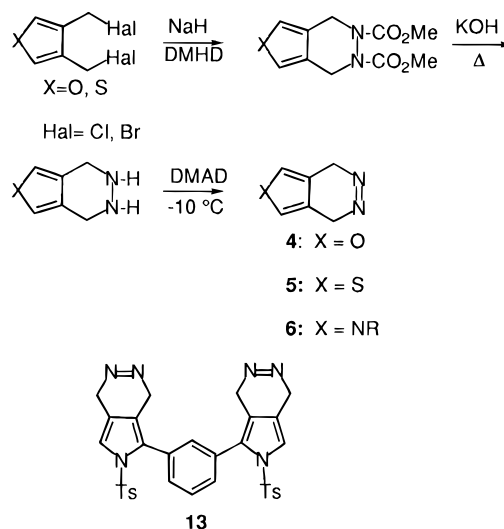
synthesis of diazene precursors of 3,4-dimethyleneheterocycles. We hoped to apply analogous chemistry to the case of the tetraradicals **10**−**12**, and accordingly, our initial goal was a versatile synthesis of *m*-phenylene-linked bis-diazenes (*e.g.,* **13**), which would allow for variations of the heterocycle.

Palladium-Catalyzed Cross-Coupling of Pyrroles with 1,3-Dihalobenzenes. Synthesis of Bis-Diazene 13. After indifferent success (described elsewhere[6b]) in a few initial attempts to prepare difuryl-, dithienyl-, and dipyrrylbenzenes by adaptation of classical methods[9] of 1,4-dicarbonyl cyclization, we learned of a successful organometallic coupling of pre-formed heterocyclic and phenyl moieties by Pelter and co-workers.[10] These authors had prepared 1,3- and 1,4-difurylbenzenes by the cross-coupling of 2 mol of 2-furylzinc chloride (obtained from furan by lithiation and subsequent treatment with zinc chloride) with 1,3- or 1,4-dibromobenzene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium. Encouraged by this work, we sought to generalize the cross-coupling reaction to accommodate variations in the structure and substituents of the heterocyclic ring. We found the procedure very sensitive to changes in the structure of the heterocycle, and separate careful optimizations of the reaction conditions were necessary for each heterocyclic system. Procedures for the furan and thiophene series are described elsewhere.[6] Scheme 2 outlines our current procedure for the pyrrole series.

We chose as the heterocyclic coupling unit 3,4-bis(methoxymethyl)-*N*-*p*-toluenesulfonylpyrrole **14** (Scheme 2), prepared from the known[1] 3,4-bis(hydroxymethyl)-*N*-tosylpyrrole. However, metallation of the pyrrole α positions of **14** by direct lithium-for-hydrogen exchange seemed unlikely to be successful. For example, *N*-*p*-toluenesulfonylpyrrole, when treated with *n*-butyllithium or *tert*-butyllithium, has been reported[11] to suffer cleavage of the *p*-toluenesulfonyl (tosyl) group. One might hope that lithium-for-halogen exchange in an α-halogenated derivative of **14** might be sufficiently fast to compete succesfully with tosyl cleavage. To test this idea, we prepared 2-bromo-3,4-bis(methoxymethyl)-*N*-*p*-toluenesulfonylpyrrole (**15**) from **14** by a known[12] low-temperature bromination procedure (Scheme 2). Satisfactory α-metallation in fact was achieved when **15** was

(5) See *inter alia*: (a) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Chapter 13 and references cited therein. (b) Whangbo, M.-H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; Vol. II. (c) Salaneck, W. R., Lundström, I., Rånby, B., Eds. *Conjugated Polymers and Related Materials*; Oxford: New York, 1993. (d) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271,* 1705 and references cited therein.

(6) (a) Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1996**, *118,* 265. (b) Lu, H. S. M. Ph.D. Dissertation, Yale University, New Haven, CT, 1994.

(7) (a) Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Phil. Soc.* **1940**, *36,* 193. (b) Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc.* **1947**, *A191,* 39. (c) *Ibid.* **1947**, *A192,* 16. (d) *Ibid.* **1947**, *A193,* 447. (e) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18,* 265.

(8) (a) Schlenk, W.; Brauns, M. *Chem. Ber.* **1915**, *48,* 716. (b) Review: Berson, J. A. In *The Chemistry of Quinonoid Compounds, Vol II*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1988; Chapter 10.

(9) For reviews, see: (a) Sundberg, R. J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A., Ed.; Pergamon Press: Oxford, U.K., 1984; Chapter 3.06. (b) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Academic Press: London, 1977. (c) Patterson, J. M. *Synthesis* **1976**, 281.

(10) (a) Pelter, A.; Rowlands, M.; Clements, G. *Synthesis* **1987**, 51. (b) Pelter, A.; Rowlands, M.; Jenkins, I. H. *Tetrahedron Lett.* **1987**, *28,* 5213.

(11) Anderson, Jr.; Freenor, F. J. *J. Org. Chem.* **1972**, *37,* 624.
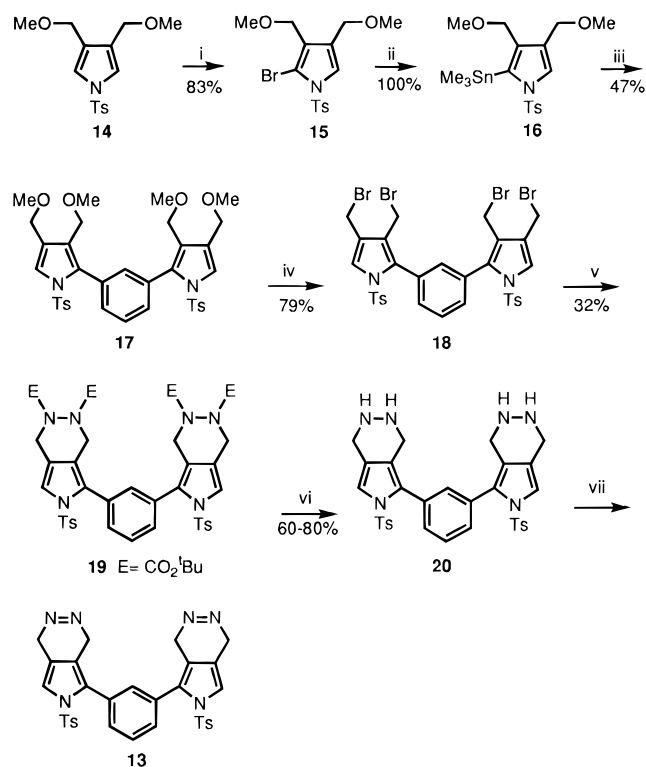
(12) Gilow, H. M.; Burton, D. E. *J. Org. Chem.* **1981**, *46,* 2221.

Scheme 2[a]

[a] **Methods**: i. NBS, −78 °C. ii. (a) nBuLi, −78 °C; (b) SnMe₃Cl. iii. 1,3-diiodobenzene/(CH₃CN)₂PdCl₂. iv. Br₂PPh₃. v. Di-*tert*-butyl-hydrazodicarboxylate, K*t*OBu, 18-crown-6. vi. HCl (g). vii. DMAD, −30 °C.

treated with *n*-butyllithium at −78 °C, followed by quenching with trimethyltin chloride to give 2-(trimethylstannyl)-3,4-bis-(methoxymethyl)-*N*-*p*-toluenesulfonylpyrrole (**16**) in quantitative yield.

The trimethylstannyl derivative **16** was more stable than the zinc derivative and could be isolated as an orange oil. Coupling of **16** with 1,3-diiodobenzene in the presence of tetrakis-(triphenylphosphine)palladium required a higher temperature (140 °C) than those used[6] in the coupling of the zinc reagents in the corresponding furyl or thienyl series (55−60 °C), and consequently, a considerable amount of polymerized material was formed. The bis-cross-coupled product **17** was obtained in only 14% yield. However, in the presence of the more reactive catalyst bis(acetonitrile)palladium(II) chloride,[13] reaction took place at room temperature and gave the desired product **17** in 47% yield. Subsequent transformations (Scheme 2) to the bis-diazene **13** were uneventfully analogous to those[6] in the furan and thiophene series. Like the diazene precursors **24**−**26** of the mononuclear 3,4-dimethylenepyrroles **21**−**23**,[1,2] the bis-diazene **13** was thermally unstable in solution at room temperature and usually was handled at a temperature of −30 °C or lower.
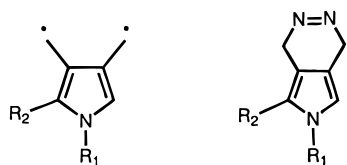
21: R₁ = Ts, R₂ = H   24: R₁ = Ts, R₂ = H

22: R₁ = Bs, R₂ = H   25: R₁ = Bs, R₂ = H

23: R₁ = Ts, R₂ = Ph   26: R₁ = Ts, R₂ = Ph

Scheme 3
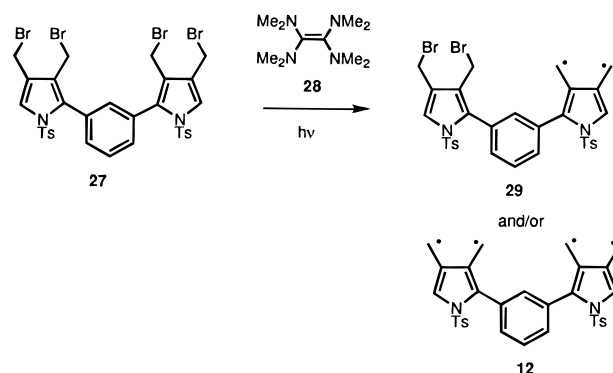
Photodeazetation of the Bis-Diazene 13 at 370 nm. Previous syntheses[1b,2d] of the singlet and triplet forms of the *N*-arenesulfonyl-3,4-dimethylenepyrroles **21**−**23** (Ts = *p*-toluenesulfonyl, Bs = *p*-bromobenzenesulfonyl) took advantage of the wavelength-dependence of the photodeazetation of the corresponding diazenes **24**−**26**, respectively. Typically, irradiation at 370 nm produced the strongly colored, ESR-silent singlet biradical, whereas irradiation at 265 nm led to the ESR-active triplet. Another ESR-active species, tentatively assigned as a diazenyl biradical, could be detected under certain conditions in the 370- and 265-nm photolyses and was formed most efficiently at 345 nm.

This approach now serves as a model for the bis-deazetation of **13**, the precursor of tetraradical **12**. Immobilized in 2-methyltetrahydrofuran (MTHF) at 77 K, the precursor bis-diazene **13** showed strong UV−vis absorptions with λ_{max} 240, 300, and 366 nm. After 5 min of irradiation with monochromatic 370 nm light, the sample was visibly green, but the UV−vis spectrum showed only declining nonspecific absorption beyond 500 nm. Further irradiation for as long as 60 min did not increase the green color, and the UV−vis spectrum remained unchanged. Thawing the matrix caused disappearance of the green color. We suggest that the weakness of the observed absorption may be caused by efficient photobleaching of the green transient, in analogy to the photobleaching of the 3,4-dimethylenepyrrole biradicals **21**−**23**.[1] The properties of the 370 nm photolysis product from bis-diazene **13** are similar to those found[1b] for the product of 370 nm photolysis of the model diazene **26**.

A stronger UV−vis spectrum could be obtained from the tetrabromide precursor **27** by application of the photochemical electron-transfer method of Haider et al.[14] When **27** (see Scheme 3) was photolyzed with Pyrex-filtered light in the presence of tetrakis(dimethylamino)ethylene (**28**) in a MTHF matrix, the sample turned orange within 30 s. Further irradiation produced visible islands of dark green material, which disappeared irreversibly when the matrix was annealed. Under these conditions, the orange intermediate persisted, but it disappeared at higher temperature. In a control experiment, tetrabromide **27** irradiated in the absence of the amine **28** gave only the orange intermediate. A reasonable interpretation would be that the orange intermediate is an ordinary direct photoproduct, whereas the green intermediate, when formed from the tetrabromide **27** by the protocol just described, results from the electron-transfer pathway. The green preparations, by analogy to the model singlet biradicals **21** (blue), **22** (blue), and **23** (green), may

(13) (a) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138. (b) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813.

(14) (a) Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318. (b) See also ref 2c.
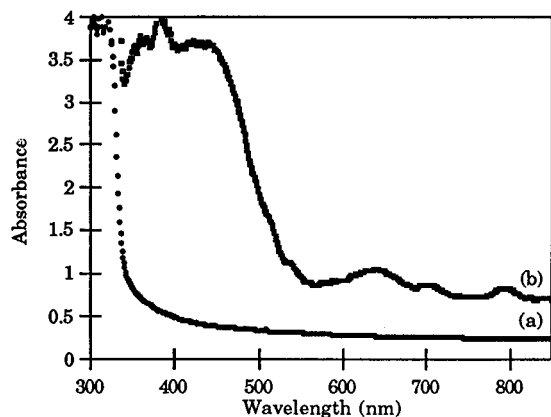
Figure 1. UV−vis spectrum obtained by irradiation of an MTHF matrix of tetrabromide **27** and tetrakis(dimethylamino)ethylene (**28**) with Pyrex-filtered light at 77 K: (a) before irradiation; (b) after irradiation. The sample contains green and orange regions after irradiation.

contain the biradical **29** and/or the tetraradical **12**, while the orange species may result from reaction elsewhere in the substrate, for example, from photodetosylation. The UV−vis spectrum (Figure 1) from the experiment of Scheme 3 shows several weak bands in the 600−800 nm region as well as a strong band between 400 and 500 nm.

It is known that, under conditions of irradiation with a 1000 W Hg−Xe arc, secondary photobleaching of the parent *N*-tosyl-3,4-dimethylenepyrrole (**21**) occurs fastest near 400 nm.[1b,2d] Thus, a likely reason for the more efficient generation of the green transient from dibromide **27** under the electron-transfer conditions than from the bis-diazene **13** may be that the strong 400−500 nm absorption, which is probably the source of the orange color, acts as an internal filter to retard the presumably similar secondary photobleaching of the green intermediate.

Of course, the use of the tetrabromide **27** as a precursor leaves open the possibility that other transient species, such as monoradicals or triradicals, may be present in these preparations. Because of the lack of detectable specific absorption in the visible region of our samples prepared from the bis-diazene **13**, we cannot be sure whether some or all of the long-wavelength bands observed in the green preparations from the electron-transfer experiment (Figure 1) are present in the spectrum of the green photolysate from bis-diazene **13**.

The ESR spectra of the orange/green samples from the tetrabromide/tetraamine (**27/28**) irradiations showed no patterns that could be attributed to a triplet or a quintet species. The only signals detected were in the center of the spectrum near 3300 G and were probably associated with the products of tosyl cleavage or other free radical impurities. The (one or more) green species from the tetrabromide **27** via Scheme 3 thus seem to be ESR-silent.

The green preparation from 370 nm irradiation of bis-diazene **13** was examined by ESR spectroscopy in glassy MTHF at 77K. A narrow four-line spectrum was observed, with $|D/hc| = 0.0132$ cm^{-1} and $|E/hc| \sim 0$ cm^{-1}. In addition, the half-field transition was observed at 1640 G. The same four-line signal could be generated from the 345 nm irradiation of bis-diazene **13**, with a higher quantum yield.

The D value of the 345/370 nm photoproduct was very similar to those of the "narrow" triplet spectra which were speculatively considered to be the diazenyl biradicals **30** ($|D/hc| = 0.014$ cm^{-1} and $|E/hc| \sim 0$ cm^{-1}) and **31** ($|D/hc| = 0.0129$ cm^{-1} and $|E/hc| \sim 0$ cm^{-1}), obtained from the 345 nm irradiation of the mononuclear diazene precursors **24** and **26**, respectively (Scheme 4).[1b,2d] The similarity of the ZFS parameters suggested that the ESR-active species obtained from 345/370 nm irradiation

Scheme 4

24: R = H   30: R = H

26: R = Ph   31: R = Ph

Scheme 5

and/or
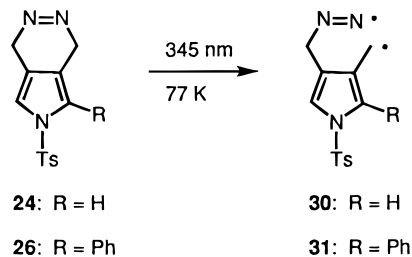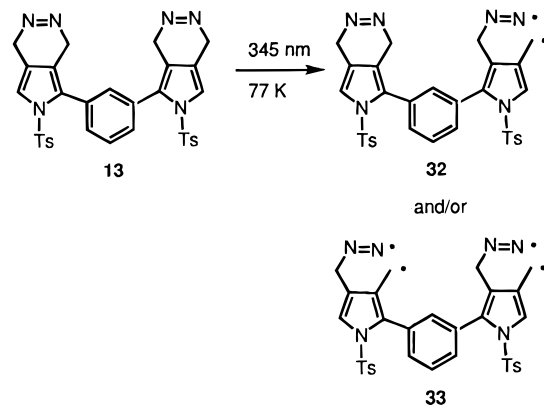
of bisdiazene **13** may be the diazenyl biradical **32** or bis-diazenyl tetraradical **33** (Scheme 5) and related isomers resulting from the homolysis of the alternative C−N bond. No evidence was found for the formation of a higher spin state of our target tetraradical **12** under these photolysis conditions.

The tetrabromide **27** (Scheme 3) is structurally incapable of generating the diazenyl (**32**) and/or bis-diazenyl (**33**) species (Scheme 5), which we think are responsible for the narrow triplet pattern formed in 345 nm irradiation of bis-diazene **13**. Thus, the absence of the narrow triplet pattern in the ESR trace of the orange-green preparations from the irradiated tetrabromide **24** (Scheme 3) is consistent with the assignments of diazenyl structures **32** and/or **33** to the carrier(s) of that pattern formed in Scheme 5.

Spectroscopic Characterization of the Product Generated from 265 nm Irradiation of Bis-Diazene 13. Analogy to observations[1b,2d] in the photochemistry of the mononuclear diazene precursors (**24−26**) of the biradicals **21−23** led us to expect that 265 nm irradiation of bis-diazene **13** in rigid MTHF matrix at 77 K would generate a colorless or yellow high-spin species with a large zero-field splitting (ZFS) parameter D. Indeed, such samples showed no visible green color, and the matrix UV−vis spectrum showed no characteristic absorptions, but even 1 min of irradiation sufficed to produce an observable ESR spectrum as an intense six-line absorption in the $\Delta m_s = 1$ region with a total width of 423 G (Figure 2). Also, the half-field transition ($\Delta m_s = 2$) was observed at 1643 G. If this signal is interpreted[15] as that of a triplet species, the ZFS can then be extracted: $|D/hc| = 0.0197$ cm^{-1}, and $|E/hc| = 0.00090$ cm^{-1}. Whether this is a necessary assignment is discussed later. Irradiation of the ESR-active sample with 400 nm light readily bleached the ESR signal, in close analogy to the behavior observed with **21−23**.[1c,2d]

The intensity of the signal of the six-line pattern continued to increase with further 265 nm irradiation for 30−45 min and

(15) (a) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1972; Chapter 10. (b) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41,* 1763. (c) Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10,* 27.
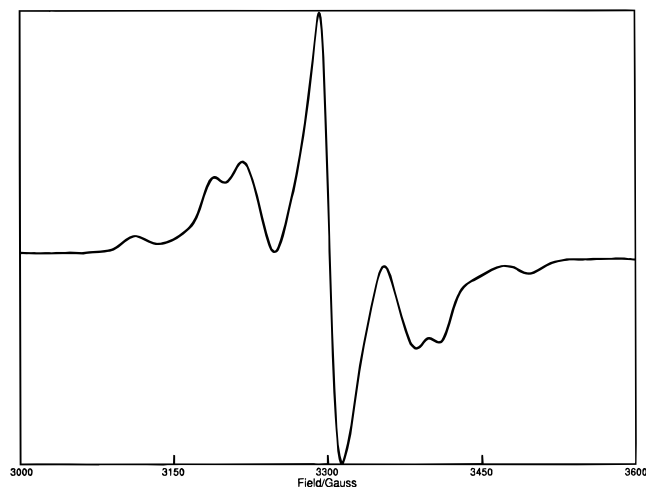
Figure 2. ESR spectrum from 265 nm irradiation of bis-diazene **13** in MTHF matrix at 77 K.

Scheme 6
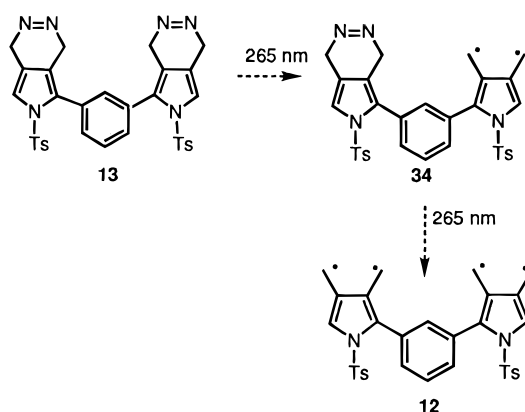
then leveled off to a steady value. Significantly, no additional signals were detected in either the $\Delta m_s = 1$ or the $\Delta m_s = 2$ region upon further irradiation. The only change in the ESR spectrum with further irradiation was in the central region around 3300 G where radical pairs and doublet impurities commonly absorb. This resonance probably was due to products of detosylation of the bis-diazene **13** or of the photoproduct.

Similar behavior was observed in irradiations at 5 K. The only detectable high-spin signal again was the same six-line triplet spectrum seen at 77 K. At 5 K, the resonance near the central region at 3300 G grew in at a much slower rate, relative to the six-line signals, than at 77 K. These experiments suggested that the triplet ESR signal observed at 77 K was not attributable to thermal population of a multiplet other than the one directly formed in the photolysis.

During the growth in intensity of the ESR spectrum formed by 265 nm irradiation, the pattern of resonances remained unchanged. This constancy was surprising, since we had expected to observe dramatic changes during photolysis. Analogy to the studies on the photochemical formation of the model biradicals **21**−**23**[1d,2c] and the stepwise formation of the thiophene tetraradical **1**[6] suggested that the photolysis of the pyrrole bisdiazene **13** would occur by stepwise deazetations and give successively the triplet monodeazetated biradical [3]**34** followed by the tetraradical **12** (Scheme 6). If the *m*-phenylene unit had behaved as a ferromagnetic coupler, the tetraradical should have existed as its quintet state, [5]**12**, which should have shown an ESR spectrum (up to 12 lines)[15−17] very different from that of the triplet precursor [3]**34** (up to six lines).

These observations raise the question whether the ESR spectrum is that of the tetraradical **12**. More specifically, the imaginable carriers of the new ESR spectrum include the monodeazetated triplet [3]**34**, the tetraradical species as a triplet [3]**12**, and the tetraradical as a quintet [5]**12**. The last of these possibilities ([5]**12**) now must be considered unlikely for several reasons, one of which (described elsewhere[6b]) is the failure of the spectrum to conform to that predicted by a quintet Hamiltonian. A second reason emerges from the spin count experiments described below, which strongly suggest that the concentration of tetraradical generated under our conditions is too small to contribute significantly to the ESR spectrum. This argues against either [3]**12** or [5]**12** as the carrier of the main spectrum.

Spin Count Experiments. The purpose of this study was to estimate the total amount of the tetraradical **12** present in the samples that gave the six-line 423 G ESR spectrum just described. In analyzing the products from the pyrrole bis-diazene **13**, the reasonable assumptions were made that (1) the photolysis of the two diazene units occurs by the sequential mechanism of Scheme 6, analogous to that observed[6] for the corresponding thiophene bis-diazene and (2) the photochemical reactivity of the diazene unit of monodeazetated biradical **34** is the same as that of one of the two equivalent diazene units of bis-diazene **13**. Since there are two reactive chromophores in **13** but only one in **34**, the quantum yield for deazetation of the the first diazene unit (reaction **13** → **34**) is assumed to be just twice that for the second diazene unit (reaction **34** → **12**).

Determinations of the concentration of paramagnetic species in a given sample were made by comparison of the ESR signal intensity to that of a glassy sample of diphenylpicrylhydrazyl (DPPH) of known concentration and volume at 77 K, according to established procedures.[17a] The ratio of the total concentration [X] of paramagnetic species in the unknown sample to the concentration [STD] of the DPPH standard sample is given by eq 1,[17a] where A_x and A_{std} are the measured areas under the

$$\frac{[X]}{[STD]} = \frac{A_x}{A_{std}} \frac{[S(S+1)]_{std}}{[S(S+1)]_x} \qquad (1)$$

absorption envelopes (obtained by double integration of the usual ESR derivative curve) of the unknown and the standard, respectively, and the terms $S(S + 1)$ are intensity factors that correct for the inherently different signal intensities of species with different spins.[17a,b] In the case here, $[S]_{std} = 1/2$, $[S]_x = 1$ for a triplet, and $[S]_x = 2$ for a quintet.

If the deazetation reaction is stepwise, at low conversions, essentially all of the sample's paramagnetism originates in the biradical **34**. However, a crucial question is whether the very small amount of tetraradical **12** present would be enough to exceed the limit of detection of the spectrometer, which is normally sensitive to concentrations of ESR-active species down to the level of 10^{-9} M.[17c] Once this criterion is satisfied, there remains the question of how much the tetraradical contributes to the observable ESR spectrum.

To estimate the concentration of **12** that is present, one can proceed by either of two formalisms which, at low conversions, should predict values that do not differ significantly for the purposes of this study. The first assumes that the degree of

(16) (a) The conditions required for the observation of extra lines in the $\Delta m_s = 1$ region are described in: Teki, Y.; Takui, T.; Itoh, K. *J. Chem. Phys.* **1988**, *88*, 6134. (b) For additional lines in the $\Delta m_s = 2$ region, see ref 15.

(17) (a) Reference 15a, pp 462−464. (b) Poole, C. P., Jr. *Electron Spin Resonance*, 2nd ed.; Wiley: New York, 1983; p 20. (c) Reference 15a, p 451.

photochemical conversion in the first step will be replicated in the second (modified only by the statistical factor of 2). Roughly then, the fraction of the monodeazetated biradical **34** converted to tetraradical **12** in the second step would be equal to one-half the fraction of the bis-diazene **13** converted to the biradical **34** in the first step, that is, $[12]/[13]_0 = 0.5\{[34]/[13]_0\}^2$. For example, if the overall conversion of the starting bis-diazene **13** were 1%, approximately 0.005% of the original **13** would be present as the tetraradical **12**.

Alternatively, and more rigorously, at low conversion, each of the steps can be treated as a first-order reaction with an exponential decay. Details of this procedure are given in the Supporting Information. Then the kinetics of such irreversible consecutive reactions[18] may be cast in the form of eqs 2–4,

$$\frac{[12]}{[34]} = \frac{1 + e^{-k_1 t} - 2e^{-k_1 t/2}}{2[e^{-k_1 t/2} - e^{-k_1 t}]}$$

$$\frac{[12]}{[34]} = \frac{1 + e^{-(\ln \theta)} - 2e^{-(\ln \theta)/2}}{2[e^{-(\ln \theta)/2} - e^{-(\ln \theta)}]} \tag{2}$$

$$\frac{[34]}{[13]_0} = 2[e^{-(\ln \theta)/2} - e^{-(\ln \theta)}] \tag{3}$$

$$\frac{[12]}{[13]_0} = [1 + e^{-(\ln \theta)} - 2e^{-(\ln \theta)/2}] \tag{4}$$

where k_1 and $k_1/2$, respectively, are the "rate constants" (functions of the quantum yields and experimental conditions) for reactions $\mathbf{13} \rightarrow \mathbf{34}$ and $\mathbf{34} \rightarrow \mathbf{12}$, respectively; θ, the ratio $[13]_0/[13]$ of the concentrations of starting **13** to the **13** after some time of photolysis, is determined from the spin count experiment. At low conversion, the concentration of **34** is very close to $[13]_0 - [13]$, and by the definition of a first-order reaction, $k_1 t = \ln \theta$.

We first carried out a model experiment in which a glassy MTHF sample of diazene **26**, the precursor of the mononuclear biradical **23**, was irradiated at 265 nm and 77 K until maximum intensity of the ESR triplet signal was achieved. The concentration of triplet species, determined from eq 1, corresponded to $0.73 \pm 0.18\%$ conversion of the starting diazene **26** to triplet biradicals, the error in the spin count measurement being estimated by known methods.[15a]

Photolysis of a glassy MTHF 0.124 M sample of bis-diazene **13**, the potential precursor of tetraradical **12**, was then carried out under the same conditions. The data of the spin count experiment, analyzed by eq 1 and the crude assumption of $[12]/[13]_0 = 0.5\{[34]/[13]_0\}^2$, would calculate $[34] = 6 \times 10^{-4}$ M and $[12] = 3 \times 10^{-6}$ M, so that the tetraradical **12** is present to the extent of only 0.5% of the ESR-active species. The more rigorous treatment of eqs 2–4 showed that, for this run, $[34] = 6 \times 10^{-4}$ M and $[12] = 1.2 \times 10^{-6}$ M, that is the tetraradical **12** constitutes only about 0.2% of the ESR-active species.

Thus it may be stated that the concentration of the tetraradical **12** in this preparation is in the micromolar range, several orders of magnitude greater than that needed to produce an observable ESR signal if the species is paramagnetic. Moreover, as is shown elsewhere,[6b] in several cases, the ESR transitions expected for $^5\mathbf{12}$ would not coincide with those of biradical $^3\mathbf{34}$, so that at even approximately comparable concentrations one could expect to observe both patterns. However, the spin count experiment shows that the concentration of **12** is so low relative

to that of **34** that detection of the pattern of **12** under the wings of the broad absorptions of **34** might be impossible. We believe, therefore, that the major carrier of the ESR signals observed from the photolysis of the bis-diazene **13** is the monodeazetated triplet biradical species **34**. Its ZFS parameters, $|D|/hc| = 0.0197$ cm^{-1} and $|E/hc| = 0.0009$ cm^{-1}, are similar to those of the model biradical **23**, $|D/hc| = 0.0187$ cm^{-1}, and $|E/hc| = 0.0005$ cm^{-1}. The slightly larger D value for **34** calls forth the suggestion that spin delocalization away from the 3,4-dimethylenepyrrole unit may be slightly greater in **23**, perhaps for conformational reasons.

In retrospect, the disappointing outcome of this attempt to generate **12** in directly observable form might have been anticipated. Bush et al.[1] already had observed similar low conversions ($\sim$1.6% by spin count) for the production of the triplet biradical **21** upon even prolonged 265 nm irradiation of its diazene **24**. The difficulty of driving this photoreaction further probably results from two factors: first, it has been speculated[1] that, in the matrix, only a small fraction of the diazene **24** is in a conformation capable of forming and supporting a triplet ground state of biradical **21**; second, the photochemistry of bis-diazene **24** is sharply wavelength-dependent. In order to produce clean specimens of the triplet **21**, the photolysis must be carried out at or near 265 nm, where the irradiance of the Hg–Xe arc is only about one-hundredth that at 370 nm.[19] Similar restrictions apply in the case of the bis-diazene **13**. Attempts to force the photoreaction of this precursor to higher conversion through the use of Pyrex- ($\lambda > 270$ nm) or band-pass (220–420 nm) filtered light gave, as expected by analogy with previous work,[1] mixtures of products.

The results in the thiophene series were more fruitful, and unambiguous evidence for the preparation and reactions of the tetraradical **11** was obtained.
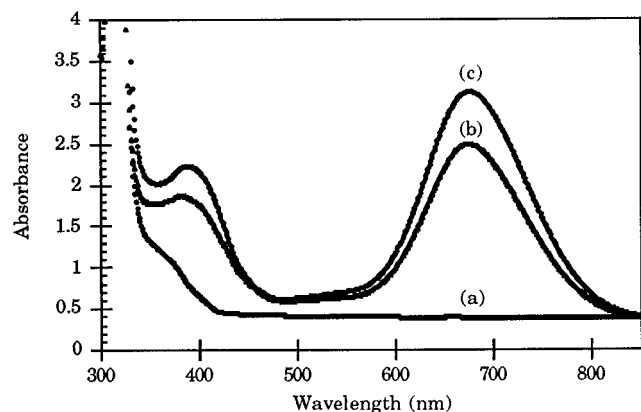
Studies in the Thiophene Series. UV–Vis Spectroscopy of Tetraradical 11. As we reported,[6] the tetraradical **11** should exist as a singlet ground state molecule and should have four nominally degenerate NBMOs. Quantum mechanical computations[6] at the semiempirical PM3-CI level[20] place these in two sets of nearly degenerate orbitals at $-119/-118$ and $-94/-92$ kcal/mol. These orbitals are the counterparts of the half-filled electron bands that would exist in the hypothetical nonclassical polymeric conductor **8**. The present effort to prepare tetraradical **11** can be considered first step toward such a polymer.

The UV–vis spectrum (Figure 3a) of a solution of bis-diazene **35**[6] (Scheme 7) in glassy MTHF at 77K showed a broad shoulder near 366 nm, presumably due to the n $\rightarrow$ * transition of the azo chromophore. Irradiation of such a glass with 350–377 nm light generated an intense green preparation. The UV–vis spectrum of the irradiated sample (Figure 3b) showed new absorptions with $\lambda_{max} \sim 386$ and 675 nm. These two bands appeared to grow in at the same rate with further irradiation (Figure 3c). There were also additional intense absorbances in the short wavelength region (<350 nm) which were observable immediately upon irradiation and quickly grew off-scale. The green color disappeared irreversibly when the matrix was thawed.

(18) (a) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism,* 3rd ed.; Wiley: New York, 1981; p 290 ff. (b) Capellos, C.; Bielski, B. H. *Kinetic Systems*; Wiley: New York, 1972; Chapter 9.

(19) *Oriel Equipment Catalog*, Vol. II, Oriel Corp.: Stratford, CT, 1994; pp 1–43.

(20) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) *Ibid.* **1989**, *10,* 221. (c) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (d) In these calculations, each methylene group of tetraradical **11** and the model biradical **38** was assumed to be planar with its thiophene ring. This assumption is supported by INDO/S-CI calculations on the model disjoint singlet hydrocarbon tetramethylenebenzene, in which the D_{2h} planar singlet lies 12 kcal/mol below the methylene-twisted (C_s) singlet.[20e] (e) Lahti, P. M. Ph.D. Dissertation (with Berson, J. A.), Yale University, New Haven, CT, 1985; Appendix 2.

Figure 3. UV−vis spectrum of thiophene bis-diazene **35** in MTHF (a) at 77 K; (b) after irradiation for 1 h; (c) after irradiation for 1.5 h.

Scheme 7
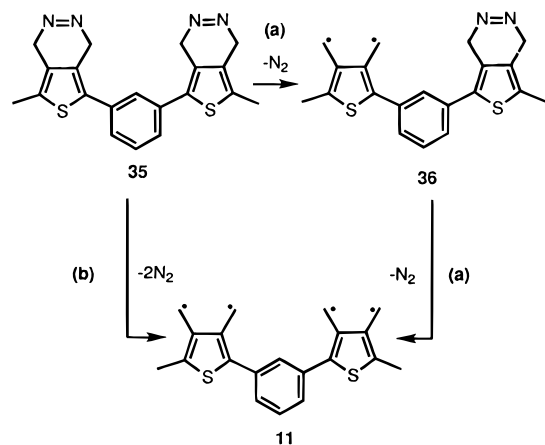
The ESR spectrum of the green matrix prepared by 77 K (or 5 K)/350−370 nm or 220−420 nm irradiation of bis-diazene **35** showed no indication of the presence of a high-spin species.

The UV−vis spectrum of the intermediate is invariant over a range of solvent, such as MTHF, ether, ethanol, and poly-(methyl methacrylate). The lack of a solvent effect suggests that there is little difference in polarity between the ground and excited states of the intermediate.

The same (by visual observation) green color appeared when the bis-diazene was photolyzed in an adamantane host. Similarly, the green color could be generated *thermally* when bis-diazenothiophene **11**, incorporated in a poly(methyl methacrylate) support, was allowed to warm to room temperature. The color of this preparation persisted for several minutes. Finally, a green transient, λ_{max} 670 nm, probably identical with the matrix-isolated species, has also been observed in solution by nanosecond laser flash photolysis studies.[1a]

Nature of the UV−Vis Carrier and Mechanism of Its Formation. Three main questions arise about the nature of the UV−vis carrier: (1) Is it the desired tetraradical **11**? (2) If so, is that species formed by sequential (Scheme 7, path a) or by simultaneous (Scheme 7, path b) release of the N$_2$ molecules from the bis-diazene **35**? (3) In the reactions—for example, trapping by alkenes—of the transients liberated by thermal or photochemical deazetation of bis-diazene **35** in fluid solution, is the reactive intermediate the monodeazetated biradical **36** or the tetraradical **11**?

In our preliminary communication and its Supporting Information,[6a] we have given the basis for our conclusions that tetraradical **11** is indeed formed by exhaustive irradiation of bis-diazene **35** *in cold matrices* and that the photodeazetation

of **35** occurs by the sequential mechanism (Scheme 7, path a). For the purpose of reference in the present paper, we give here only brief reviews of the previous evidence on these two points and add some new confirmatory information. Further, we now show that, in the *fluid solution phase,* the reactive entity is the monodeazetated biradical **36**.

Structure of UV−Vis Active Species. Presumptive evidence that one or both of the species biradical **36** and tetraradical **11** (Scheme 7) probably are involved in the photolyses is given by the structures of the cycloadducts formed when the bis-diazene **35** is deazetated in the presence of olefinic trapping agents (see below). These products are exactly analogous to those formed in the reactions of two 3,4-dimethylenethiophene derivatives, the parent compound **2**, prepared from diazene **5**,[2] and the 2-phenyl-3,4-dimethylene analogue **38**, prepared from the diazene **37**.[6a]
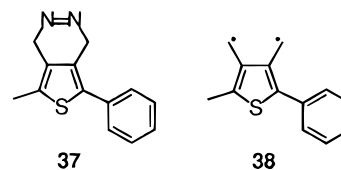

That the product **11** of exhaustive matrix photolysis of bis-diazene **36** contains *two* 3,4-dimethylenethiophene chromophores is shown by the optical extinction coefficient (ϵ) of 9700 M^{-1} cm^{-1} at the long-wavelength maximum,[6a] which is almost exactly twice that of the mononuclear models **2**[2] (λ_{max} 570 nm, $\epsilon = 5000$ M^{-1} cm^{-1}) and **38**[6a] (λ_{max} 672 nm, $\epsilon = 4800$ M^{-1} cm^{-1}). The mechanistic studies (see below) show that the product in the matrix photolyses at lower conversions consists of a mixture of monodeazetated biradical **36** and bisdeazetated tetraradical **11**.

The UV−vis spectrum λ_{max} 675, ϵ 9700 M^{-1} s^{-1} for **11** serves to rule out other possible structures, such as **39**, based on the 1,1-diazene chromophore, since authentic 1,1-diazenes[21] have very different properties: long-wavelength maxima near 500 nm and extinction coefficients <100 M^{-1} cm^{-1}.
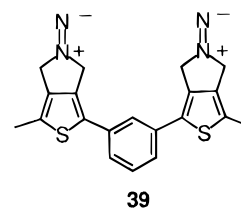

Mechanism of Deazetation of Bis-Diazene 35 Determined by Two Methods. On the question of mechanism, we note that, for other compounds, the literature reports examples of both stepwise and simultaneous deazetations. An instance of the simultaneous deazetation pathway was seen in the irradiation of 1,3-bis(α-diazobenzyl)benzene (**40**) in rigid organic glass or crystalline benzophenone host. This immediately gave the quintet dicarbene **41**, which was identified by an ESR signal whose strength depended on the second power of the irradiating light intensity.[16a,b]
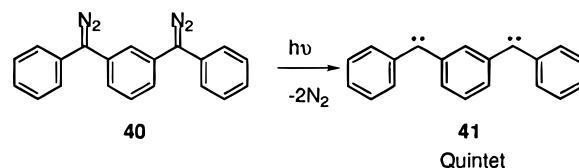
Higher members of the metaphenylene-linked poly(diazo) series also were shown to undergo simultaneous deazetation.[22a,b]

On the other hand, the deazetation of several bisdiazene precursors (*e.g.,* **42**) of tetraradicals (*e.g.,* **44**) in rigid glasses occurred by a stepwise mechanism passing over a monodeazetated biradical intermediate (*e.g.,* **43**).[22c]


Scheme 8
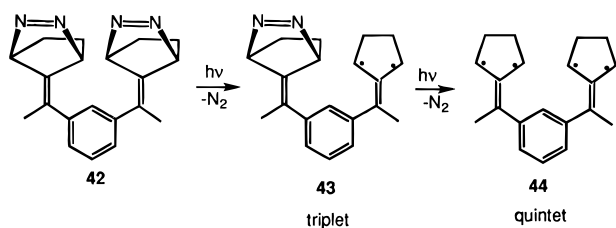
In both of these cases, the course of the deazetations could be followed by the characteristic differences in the ESR spectra of triplets and quintets.[16] However, this technique was not applicable in the present work, since the transient species generated in the matrix photolyses of our bis-diazene **35**, as singlet molecules, were expected to be and found to be ESR-inactive (see above).

We also examined UV−vis spectroscopic methods for distinguishing between the two mechanisms (a and b) of Scheme 7. The most straightforward approach depended on the hope that λ_{max} of the tetraradical **11** might be observably red-shifted from that of the biradical **36** (and that of the model biradical **38**) because of the extension of conjugation. If mechanism a of Scheme 7 operates, this would produce UV−vis spectra that gradually move to longer wavelength with increased irradiation time. Unfortunately, this was not feasible, since the maxima in the UV−vis spectra of the photolysates of bis-diazene **35** occurred at nearly the same wavelength as those of the model biradical **38**; the wavelength maximum of the preparations from irradiation of **35** in MTHF glasses at 77 K merely increased in intensity but hardly changed in position during the entire course of irradiation. That no shift was seen may be a consequence of nonplanarity of the π-system, or it may be that, even in the planar conformation, the extension of conjugation is only formal, because the meta position of the *m*-phenylene unit, where the second chromophore is linked, is a node in the HOMO. Related observations of minimal mutual chromophoric perturbations have been reported in other 1,3-linked poly(arylmethyl) radicals, anions, and radical anions.[41]

First Method. However, an alternative UV−vis method, which depended only on the intensity of the absorption, was applicable. For the stepwise mechanism (path a of Scheme 7), if it is assumed that the quantum yields for each deazetation step (**35 → 36** and **36 → 11**) are approximately equal to that for the deazetation of the model diazene **37**, photolyses of **35** and **37** for equal times under comparable conditions at conversions below the formation of one biradical unit would lead to approximately equal absorbances. In contrast, a substantial contribution from a one-photon double-deazetation mechanism for bis-diazene **35** would make the absorbance from the reaction of **35** much larger than that from **37**. As has been reported,[6a] the experimental results are compatible with the stepwise mechanism.

Second Method. Although it is a plausible assumption that the presence in **36** of one biradical unit does not affect the photochemistry of the remaining diazene unit remote from it,
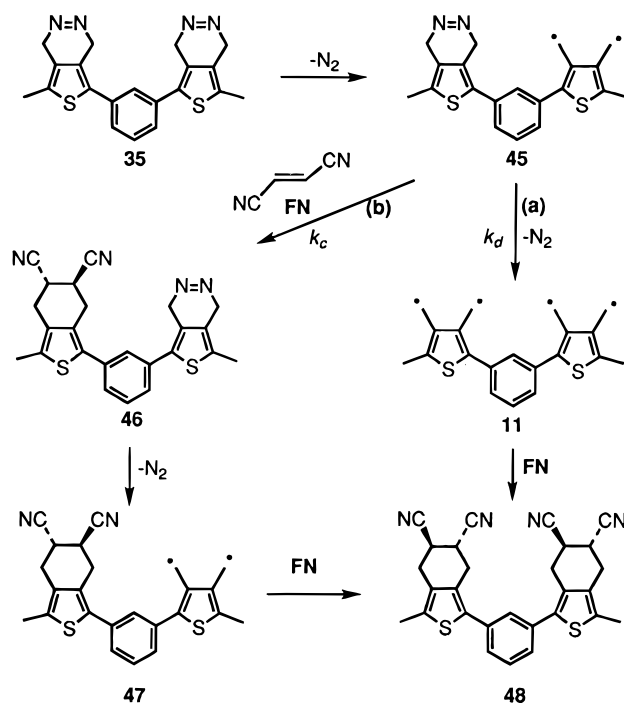
some independent evidence for it would be desirable. Therefore, a second method, free of this assumption and in fact nonspectroscopic, was developed to confirm the result. The second method uses a two-stage trapping experiment, which takes advantage of the large ratio (27:1) of reactivities of two alkenes, maleonitrile and acrylonitrile, in intercepting (see below) the photolytically generated (in glasses at 77 K) transients from bis-diazene **35**. The rationale and execution of those experiments have been described[6] and will not be repeated here, but the results confirm the stepwise mechanism.

Chemistry of the Tetraradical in Thawed Matrices Is Distinct from That of the Intermediates Generated in Fluid Medium. We assume that the stepwise mechanism demonstrated for the deazetation in matrices also applies to the photochemical deazetation in fluid solution (see below) and to the thermal deazetation. However, it should be kept in mind that the species actually undergoing reaction in the trapping reactions of the species generated from bis-diazene **35** in fluid solution are not the same as those being trapped when an irradiated glassy matrix preparation of **35** is thawed. In the latter case, after extensive irradiation to deazetate both diazene functions, the reactive intermediate is the tetraradical **11**. Under the solution phase conditions (see below), the evidence is compelling that the reactive intermediate is a biradical, either a species **45** from monodeazetation of bis-diazene **35**, or an adduct biradical **47**, from deazetation of the capture product of the diazene biradical.

Chemistry of the Transients in Fluid Solution. Deazetation of the model diazene **37** or the bis-diazene **35** can be effected either thermally (> -10 °C) or photochemically in fluid solutions. When electronegatively substituted alkenes such as maleonitrile (MN), fumaronitrile (FN), acrylonitrile (AN), etc., are included in the reaction mixture in sufficient concentration (> 0.1 M), interception products[6] (for example, **48**, Scheme 8) analogous to those observed[2] in the reactions of 3,4-dimethylenethiophene (**2**) are formed in yields of 50−85%. The kinetics of the thermal decomposition, monitored by ^{1}H NMR at 283 K, are first-order in **35** and essentially zero-order in the trapping agent, as would be expected for a reaction with a rate-determining unimolecular step. The rate constant, 2.4×10^{-4}

(21) Schultz, P. G.; Dervan, P. B *J. Am. Chem. Soc.* **1982,** *104,* 6660 and references therein.

(22) (a) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986,** *108,* 2147. (b) Sugawara, T.; Inada, M.; Iwamura, H. Tetrahedron Lett. **1983,** *24,* 1723. (c) Dougherty, D. A.; Jacobs, S. J.; Silverman, S. K.; Murray, M. M.; Schultz, D. A.; West, A. P., Jr.; Clites, J. A. *Mol. Cryst. Liq. Cryst.* **1993,** *232,* 289.

s^{-1} (at 283 K), remains steady over almost 3 half-lives, which indicates that the rates of release of the first and second molecules of nitrogen are virtually equal.

A mechanistic question about the thermal deazetation now arises (Scheme 8): Once the first molecule of nitrogen is lost from the bis-diazene **35**, does the intermediate biradical diazene **45** lose the second molecule of nitrogen (path a) to give the tetraradical **11**, which is then captured, or alternatively, is the biradical diazene **45** first captured (path b) by the trapping agent (FN, for example), which only then loses the second molecule of nitrogen? The issue here is not the one considered before, namely whether both N$_2$ molecules come out simultaneously, but rather whether the second step of the sequential mechanism for N$_2$ release can compete with capture of the intermediate stage (biradical diazene **45**) in the deazetation sequence. The answer requires an estimate of the ratio $k_c[FN]/k_d$, where [FN] is the concentration of the trapping agent FN. We make the plausible assumptions that k_c, the absolute rate constant for the capture of the monodeazetated biradical **36** by FN, is approximately the same as that measured[2e−g] for the parent biradical of the thiophene series, **2**, about 10^8 M^{-1} s^{-1}, and that k_d, the rate constant for loss of the second nitrogen from biradical **36**, is about the same as that of the first nitrogen, 2.5×10^{-4} s^{-1} at 283 K. Thus, at 0.1 M [FN], the rate of capture of the biradical **45** would be about $10^9−10^{10}$ times faster than its deazetation, a ratio so overwhelming that our assumptions could be in error by orders of magnitude without affecting the major conclusion: *under thermal conditions in fluid medium,* the formation of trapping product **48** occurs largely by path b, and tetraradical **11** is not an important intermediate.

The observed steady rate constant for thermal deazetation of bis-diazene **35**, which signifies near-equality of the rates for loss of the first and second molecules of N$_2$, then means that the deazetation of the monoadduct-monodiazene **46** has about the same rate as that of the bis-diazene **35**. As might have been expected, the remote substituent (azo function in the bis-diazene **35** or carbocyclic function in the cycloadduct **46**) has little effect on the rate of deazetation.

Structure **48** shows one enantiomer of the racemate obtained as one of the trapping products from FN. Also formed in roughly equal amount is the corresponding meso compound. No other product isomers are observed. Similarly, with MN, only a racemate and a meso compound are formed, both different from and uncontaminated by the FN adducts (HPLC analysis). The addition reaction is thus completely stereospecific. It is also regiospecific for fused addition, since ^{1}H NMR analysis of the crude adduct mixtures showed that bridged adducts such as **49** were entirely absent. This matches the behavior of the parent 3,4-dimethylenethiophene **2**,[2a−c] which also gives regiospecific fused addition to alkenes.
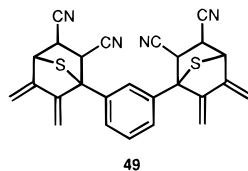

49

Chemistry of the Tetraradical 11 in Thawed Matrices. Extensive irradiation, monitored by UV−vis spectroscopy, of frozen MTHF matrices containing bis-diazene **35** and an alkene trapping agent, was carried to >95% of complete deazetation to generate an immobilized mixture of tetraradical **11** and alkene. When the matrix was thawed, the same adducts observed in the solution reactions were observed in yields of 57% from FN and 61% from MN.

Table 1. Relative Reactivity of Various Pairs of Olefins with Tetraradical **11** in Thawed Matrices

[**35**], mM	[olefin X], M	[olefin Y], M	counts of X−X[a]	counts of Y−Y[a]	k_{rel}[b]	k'_{rel}[c]
1.4	[DMF] 0.071	[MN] 0.073	7650585	2485222	1.80[d]	246
1.4	[FN] 0.31	[MN] 0.29	2412647	1146286	1.38	189
	MN	MN	−	−	1.00	135
1.3	[AN] 5.6	[MN] 0.037	5898504	187301	0.037	5
1.4	[DMM] 1.3	[MN] 0.039	312963	547442	0.0073	1.0

^{a} X−X represents the products obtained from trapping 2 mol of olefin X, and Y−Y represents the products obtained from trapping 2 mol of olefin Y. ^{b} $k_{rel} = k_{olefin X}/k_{olefin Y}$ as determined from eq 5. ^{c} k'_{rel} with respect to DMM. ^{d} The trapping reaction in this case was carried out under thermal conditions in fluid medium.

Thus the intermolecular cycloaddition products of the tetraradical **11** can be obtained in moderate to good yields, despite the formal possibility of a competing intramolecular process, the cyclization by junction of two of the radical centers of **11** to give the biradical **50**. We have not found products in these

**11**   **50**
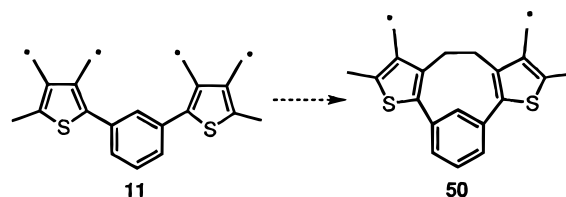
reactions that can be attributed to **50**, although we cannot rule out the presence of such products in the reaction mixture. The simplest interpretation is that the intramolecular cyclization to **50** is slow in comparison to the cycloaddition (or conceivably, it is reversible). Just how slow the cyclization can be is suggested by a comparison with the rate of cycloaddition. Although the absolute rates of capture of **11** have not been measured, data for the parent 3,4-dimethylenethiophene (**2**) are available.[2e−g] If we assume for a rough estimate that the rate constant for capture of tetraradical **11** is the same as that of the biradical **2**, 1.1×10^8 L mol^{-1} s^{-1}, the actual rate under the experimental conditions of the trapping reaction (0.127 mM FN) would be 1.4×10^7 s^{-1}. At most, products from **50** could account for 43% of the tetraradicals generated, so that (43/57) $\times$ (1.4×10^7) s^{-1} or about 1×10^7 s^{-1} is an upper limit for the rate of cyclization. This is an exceptionally slow rate for the *intramolecular* combination of two radicals. A major cause of this must be the high strain energy of **50**, which has a formal trans double bond in a nine-membered ring, seven of whose carbons are trigonally bonded.

Relative Reactivities of Tetraradical 11 by Competition Experiments. Thawing of an extensively irradiated matrix containing bis-diazene **35**, together with *two* trapping alkenes in large excess and known ratio, permits the determination of the relative reactivities of the alkenes in competition for the tetraradical **11**. Under these conditions, the products are of two types: homogeneous, in which both alkene moieties are the same, and mixed, in which one molecule of each of the trapping alkenes is incorporated. The mixed adducts, which generally emerge with HPLC retention times intermediate between the two homogeneous adducts, can be recognized by their absence when either competing alkene is used alone and by their mass spectra when the competition is between non-isomeric alkenes.

Complete analysis of the complex mixtures obtained was impractical, and accordingly, we calculated the reactivity ratios using only the HPLC peaks of the homogeneous adducts **P$_{1−1}$** and **P$_{2−2}$** (Scheme 9 and Table 1). Our interpretation of the data assumed that the rate of reaction of the tetraradical **11** (two

Scheme 9
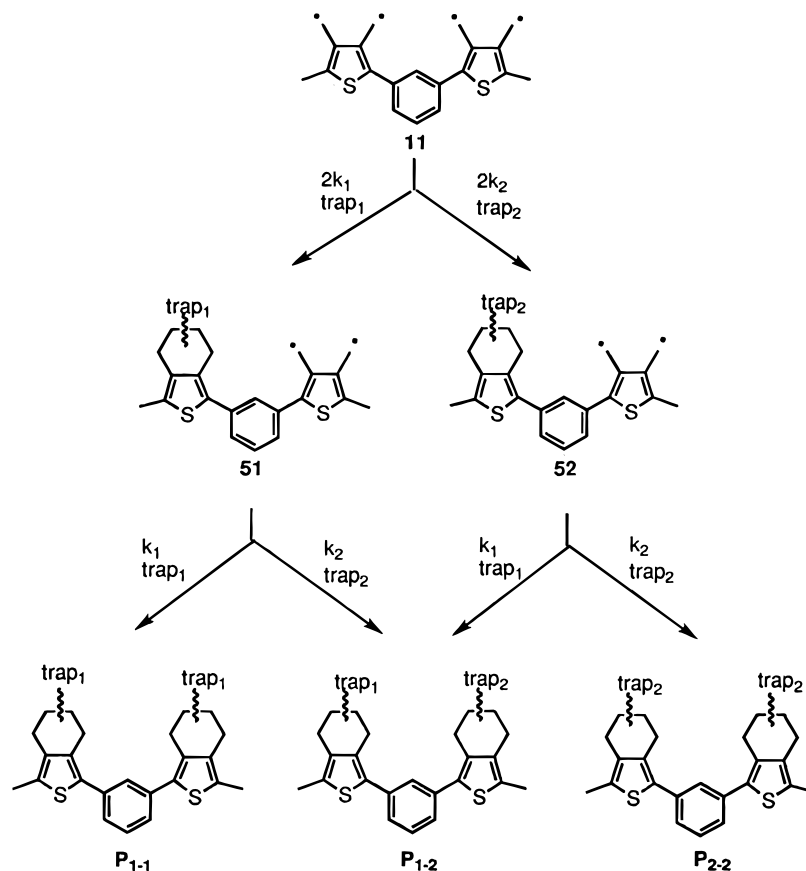
reactive sites) with a given alkene is just twice that of the reaction of the adduct biradical (one active site) with the same alkene, that is only a statistical factor differentiates the rates, and the presence of the alkene moiety in the adduct biradical has no other effect. This is probably not strictly correct, since small steric and other structural differences would be expected, but as is shown below, the assumption cannot be grossly in error. Application of the steady-state approximation to the concentrations of the intermediate adduct biradicals **51** and **52** then gives eq 5, which expresses the experimentally determined product ratios in terms of the trapping rate constants k_1 and k_2.

$$\frac{\mathbf{P_{1-1}}}{\mathbf{P_{2-2}}} = \frac{k_1{}^2[\text{trap}_1]^2}{k_2{}^2[\text{trap}_2]^2} \qquad (5)$$

Solution of eq 5 for the pairwise competitions gives the series of relative rate constants: dimethyl fumarate, 246; fumaronitrile, 189; maleonitrile, 135; acrylonitrile, 5; dimethyl maleate, 1. When the defined point (DMM) is omitted, these relative rates correlate quantitatively ($r = 0.99$) in a logarithmic plot with those[2b] for capture of the parent 3,4-dimethylenethiophene biradical **2** (Figure 4).

The agreement of the two series of relative rates supports the assumption that the rate constants k_1 and k_2 for the second steps of Scheme 9 may properly be obtained by statistical adjustment of the rate constants $2k_1$ and $2k_2$ of the first steps. This in turn strongly suggests that the reactivity at one biradical reactive site of the tetraradical **11** is not appreciably influenced by the presence of the other biradical site.

Conclusions and Prospects. Flexible methods for the catenation of 3,4-dimethyleneheterocycles of the furan, pyrrole, and thiophene series have led to the synthesis of bis-diazene precursors of *m*-phenylene-linked tetraradicals. In the pyrrole
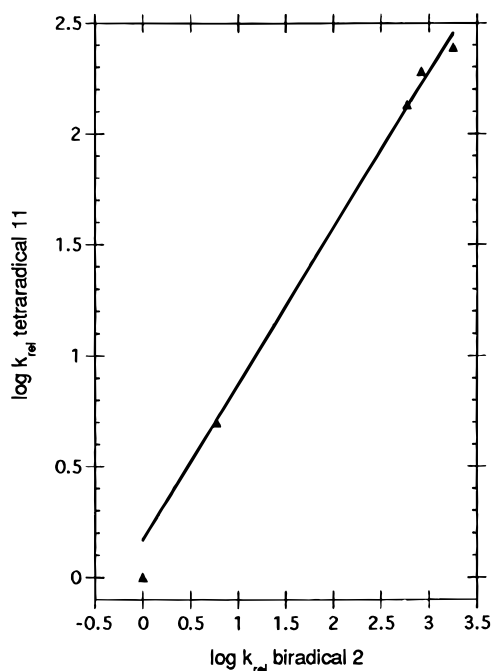
Figure 4. Relative reactivities of biradical **2** in fluid solution and tetraradical **11** in a thawed MTHF matrix (see also Table 1).

series, 265 nm matrix photolysis of the bis-diazene proceeds in only 0.5% conversion (spin-count) to give the monodeazetated triplet biradical, which is recognized by its characteristic ESR spectrum. The tetraradical is present only to the extent of 0.2– 0.5% of the biradical and, therefore, cannot be observed directly by ESR under these conditions. Eventual use of this type of catenation for the construction of high-spin systems will require

a precursor with a much higher quantum yield for photoconversion to the polyradical.

In the thiophene series, the bis-photodeazetation can be driven to completion, and the intensely green singlet tetraradical **11** can be characterized by UV−vis spectroscopy and by its characteristic cycloaddition reactions with alkenes. Potentially useful in a practical sense is the observation that the tetraradical also can be generated thermally from the bis-diazene **35** and persists for a significant time even up to room temperature in a hard matrix.

Tetraradical **11** is a prototype of polymeric species such as **8**, which embody the structural motif of a nonclassical conductor. We believe that this type of polyradical merits further study as a potential molecular wire. Of course, many unsolved problems remain before the fabrication of such wires can become practical. One major property of potential polymeric conductors which frequently is unknown or predicted with difficulty is the specifically solid-state intermolecular interactions between or among chains, which can be decisive in the ultimate bulk conductivity.[5] This feature is common to all such systems.

However, there is another problem inherent uniquely to the single-molecule level of the nonclassical polymeric conductors: is it true that the weakly bound frontier electrons in the "half-filled" NBMOs really are exceptionally favorable to high conductivities? Although actual synthetic accessibility now seems likely, we suggest that, before a major investment of effort is made toward the synthesis of these polymers, it would be advisable to have some experimental confirmation that the nonclassical structure will in fact confer high conductivity on the isolated chain of such a system. We propose, in other words, that a comparison be made of the actual conductivity of an oligoradical of type **8** with that of a model *m*-linked dithienylbenzene oligomer of conventional structure lacking the "half-filled" NBMO feature. The objective would be to isolate for examination the specifically *intramolecular* contribution of the nonclassical structure to the conductivity. One approach might be based upon recent experimental advances[5d] which have permitted the determination, by scanning tunneling microscopy, of conductivities of classical single molecular wires inserted into *n*-dodecanethiol self-assembled monolayers on a gold surface. These results offer the hope that the experiments proposed here for the nonclassical species also could be done.

Experimental Section. See the Supporting Information.

Supporting Information Available: Text describing the synthesis of pyrrole bis-diazene **13**, spin count, and kinetic analysis of its photolysis products (10 pages). See any current masthead page for ordering and Internet access instructions.