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1,3-Bis(3,4-dimethylene-5-methyl-2-thienyl)benzene, a Singlet Tetraradical Prototype of a Quasi-Alternant Nonclassical Conducting Polymer

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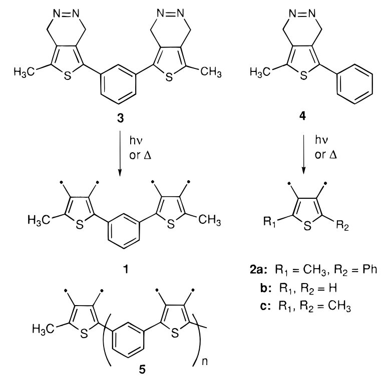
π-Conjugated heteroatom-substituted non-Kekulé compounds[1,2] are attractive building blocks for the construction of polymers with a half-filled band of nominally nonbonding molecular orbitals (NBMOs). The polymers derived from triplets or higher odd multiplets should be (magnetic) insulators, but the polymers from singlets should have metallic conductive properties.[3] Recent generalizations[4] of the Coulson−Rushbrooke−Longuet-Higgins theorem[5] to nonalternants and to heteroatomically substituted conjugated systems guide the proper linkage of the monomer units into an array with an NBMO-rich energy spectrum. These considerations motivate the present syntheses (Scheme 1)[6] of the title tetraradical **1** and, for comparison purposes, the model biradical **2a** (a derivative of the known[1c,e] 3,4-dimethylenethiophene **2b**) from the corresponding diazenes **3** and **4**. The tetraradical **1** is a quasi-alternant[4] in which two singlet biradicals are linked through an appropriate spacer to embody the structural motif of a nonclassical[4] conducting polymer **5**.

In the solution phase in the presence of alkenic trapping agents, thermal (> -10 °C) or direct photochemical deazetation of either the diazene **4** or the bis-diazene **3** gave rise to good yields of fused cycloaddition products analogous to those observed previously from the parent 3,4-dimethylenethiophene **2b**[1c,e] and its 2,5-dimethyl analog **2c**.[1d] With stereochemically defined alkenes (maleonitrile, fumaronitrile, diethyl fumarate), the reactions were stereospecifically syn.

The kinetics of the thermal deazetation of **3**, studied at 283 K by ^{1}H NMR spectroscopy (CDCl$_3$ solvent with CH$_3$CN internal standard), were first-order in diazene and zero-order in alkene, consistent with unimolecular formation of a reactive intermediate as the rate-determining step.

Relative reactivities of the model biradical **2a** and the species derived from the bis-diazene **3** toward alkenes were determined by competition experiments. It was assumed that both biradical units generated from **3** reacted at the same rate. For **2a** (photochemical generation), the relative reactivities were fumaronitrile (FN) 123 and acrylonitrile (AN) 1.0. For the species from bis-diazene **3** (thermal conditions), the values were dimethyl fumarate (DMF) 240, FN 185, maleonitrile (MN) 135, AN 5, and dimethyl maleate (DMM) 1.0. The relative reactivities of the alkenes with the transient species from diazenes **3** and **4** are similar to those found[1] in reactions with other 3,4-dimethylene heterocycles, in which frontier orbital interactions determine the reactivity order.

Scheme 1



The model biradical **2a** was generated for direct observation as an ESR-silent (5-77 K) green transient, λ_{max} 382 and 672 nm (compare the parent **2b**, λ_{max} 570 nm[2b]) when a frozen glass (77 K) of diazene **4** in 2-methyltetrahydrofuran (MTHF) was irradiated with 350 nm light (Rayonet reactor). The color and spectrum of **2a** survived in the dark at 77 K but disappeared rapidly when the glass was allowed to melt. Photoconversion of the diazene **4**, as monitored by ^{1}H NMR spectroscopy at −78 °C, was carried to completion (>95%). With the assumption[1b] that the formation of **2a** is the only pathway of photodecomposition of diazene **4**, an extinction coefficient of 4800 M^{-1} cm^{-1} was determined for the 672 nm band of biradical **2a**.

Similar photolysis of a dilute frozen solution of the bis-diazene **3**, λ_{max} ~366 nm, with 350−377 nm light again formed an ESR-silent green glass, λ_{max} ~386 and 675 nm. The extinction coefficient of the 675 nm band from photolysis of bis-diazene **3** was 9700 M^{-1} cm^{-1}, almost exactly double that of the model biradical **2a**. This leaves little doubt that both diazene units of **3** had reacted and that the carrier of the UV−vis spectrum was tetraradical **1**.

The 675 nm band of **1** also can be observed as a transient on the nanosecond time scale by laser flash photolysis.[7] The green color of the photochemically generated singlet tetraradical **1** persists in adamantane matrix up to 198 K. Tetraradical **1** apparently also can be generated thermally: warming a poly(methyl methacrylate) film of bis-diazene **3** to room temperature gives a green color which persists for several minutes.

For both practical and theoretical reasons, it is important to know whether the photodeazetation of the bis-diazene **3** in matrices occurs by a simultaneous or a stepwise sequential mechanism. The literature of diazo and azo photochemistry contains examples of both pathways.[8] Studies of the mechanism of the photo-bis-deazetation of **3** cannot apply to ordinary searches for characteristic spectroscopic absorption regions, since the positions of the UV−vis bands of the mono- and bis-deazetated products from **3** are nearly the same, and since no ESR spectra appear for these transients. We therefore have developed two new tests.

In the first, the changes in the UV−vis absorbance at 675 nm associated with the green transients from **3** or **4** were monitored as a function of irradiation time of MTHF glasses

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[1] (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. *J. Am. Chem. Soc.* **1989**, *111*, 3671. (d) Haider, K. W.; Clites, J. A.; Berson, J. A. *Tetrahedron Lett.* **1991**, *32*, 5345. (e) Scaiano, J. C.; Wintgens, V.; Haider, K.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8732. (f) Heath, R. B.; Bush, L. C.; Feng, X. W.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.* **1993**, *97*, 13355.

[2] (a) Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273. (b) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 8086. (c) Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 930.

[3] (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.

[4] Tyutyulkov, N.; Karabunarliev, S.; Ivanov, C. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 139 and references cited therein.

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

[6] (a) Described in the supporting information to this paper and elsewhere.[6b] (b) Lu, H. S. M. Ph.D. Dissertation, Yale University, New Haven, CT, 1994, p 48 ff.

[7] Heath, R. B.; Berinstain, A. B.; Scaiano, J. C.; Lu, H. S. M.; Berson, J. A. Unpublished observations.

[8] (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.

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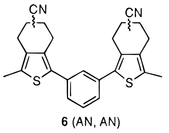
Table 1. Absorbance as a Function of Photolysis Time at 350 nm and 77 K for MTHF Glasses of Diazene **4** and Bis-Diazene **3**

	photolysis time, min	absorbance at 675 nm	no. of biradical units formed[a]
diazene **4** (0.47 mM)	15	0.51	0.71
	30	0.68	0.94
	45	0.70	0.97
bis-diazene **3** (0.47 mM)	15	0.56	0.73
	30	0.74	1.03
	45	0.87	1.21

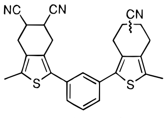
[a] Calculated using $\epsilon = 4800$ M^{-1} cm^{-1}.

initially 0.47 mM in diazene. For the stepwise mechanism, if it is assumed that the quantum yield for each deazetation step is approximately equal to that for the deazetation of **4**, photolyses of **3** and **4** for equal times under comparable conditions at conversions below the formation of one biradical unit would lead to equal absorbances. In contrast, a substantial contribution from a simultaneous one-photon double deazetation mechanism for bis-diazene **3** would make the absorbance from the reaction of **3** much larger than that from the reaction of **4**. The experimental results in Table 1 fit the stepwise rather than the simultaneous mechanism.

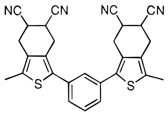
A confirmatory result was obtained in the second test, a two-stage trapping experiment, which takes advantage of the difference in reactivity of two olefinic trapping agents. Several identical tubes containing MTHF solutions of bis-diazene **3** and AN were frozen and irradiated at 77 K for differing times. The tubes were warmed to 196 K (first stage), permitting the AN to trap the photochemically generated transients as adduct **6** (AN, AN). Then a fast trap, maleonitrile (MN), which is 27 times as reactive as AN toward the model biradical **2a** (see above), was added to the cold solution. The sample was allowed to warm to room temperature (second stage), where thermal deazetation of any remaining diazene units is fast. This second (purely thermal) trapping reaction, regardless of whether deazetation of **3** is simultaneous or stepwise, gives a product distribution of adducts determined by the now known relative rates of reaction of AN and MN and the relative concentrations of these olefins.



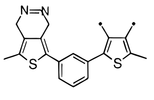
6 (AN, AN)



7 (MN, AN)



8 (MN, MN)



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If the original photodeazetation of **3** were simultaneous, the only source of the adducts **7** (MN, AN) and **8** (MN, MN) would be the thermal second stage of the experiment. These adducts would be formed from common intermediates, and their ratio would be *independent* of the extent of photoconversion (as measured by first-stage irradiation time). On the other hand, if photodeazetation of **3** were stepwise, the adduct **7** (MN, AN) would be derived from two sources: (1) thermally from unreacted diazene **3** and (2) from a sequence initiated by trapping the photochemically generated mono-deazetated intermediate **9**. The source of adduct **8** (MN, MN) would still be purely thermal. Thus, the ratio of adducts **7** (MN, AN):**8** (MN, MN) should be *time-dependent*, increasing with longer irradiation. (The supporting information gives further details.) Adduct **8** (MN, MN) in the two-stage experiment should decrease with photoconversion in either mechanism; adduct **7** (MN, AN) should decrease with photoconversion in the simultaneous mechanism but increase to a plateau in the stepwise mechanism. Figure 1 shows experimentally that, with increased photoconversion, the **7:8** ratio increases, the yield of **8** decreases, and the yield of **7** increases, as predicted by the stepwise mechanism.

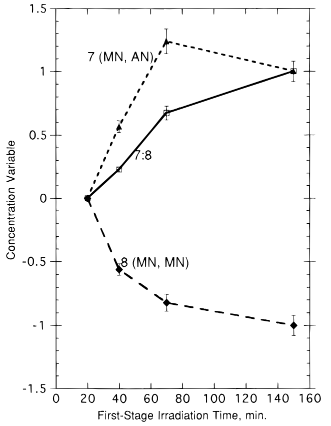

Figure 1. Two-stage trapping experiment. HPLC data for products after the second-stage step as a function of irradiation time in the first stage. The concentration variable is the fraction of the total variation $(A_t - A_i)/(|A_f - A_i|)$, where the HPLC area (or area ratio) terms refer to time *t*, initial time *i*, and final time *f*.

It is of interest that, even at low photolysis time, substantial amounts of the adduct **6** (AN, AN) are formed. Tetraradical formation by bis-deazetation in the stepwise mechanism thus seems to be a facile photoreaction, a property that should be favorable in eventual application to the synthesis of the multiradical **5**.

PM3-CI[9a,b] and AM1-CI[9c] calculations indicate that the lowest triplet states of the model biradical **2a** and of the tetraradical **1** lie 5.7 and 5.8 kcal/mol, respectively, above the corresponding singlets. The quintet of **1** lies 11 kcal/mol above the singlet. Thus, even at room temperature, little population of the higher multiplet states can be expected. This is in accord with the observed absence of ESR signals in these species and also with the complete syn stereospecificity of their cycloaddition reactions with alkenes.

The number of nominal NBMOs per 3,4-dimethylenethiophene unit in an oligomer of type **5** (*n* is small) is ≥ 1 by the quasi-alternant theorem[4] and actually is 2. At the PM3-CI level, these orbitals in the model singlet biradical **2a** have energies of -118 and -93 kcal/mol. The singlet tetraradical **1** has four nominal NBMOs in two sets of nearly degenerate orbitals: $-119/-118$ and $-94/-92$ kcal/mol. These sets of orbitals in the prototype are counterparts of the half-filled electron bands that would exist in a nonclassical polymeric conductor constructed on these principles (**5**, *n* is large).[10]

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Supporting Information Available: Synthesis of diazene **4** and bis-diazene **3**, trapping experiments, photochemistry, and spectroscopy and details of molecular orbital calculations (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(9) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, (b) 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 **1** and **2a** 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.[9e] (e) Lahti, P. M. Ph.D. Dissertation (with Berson, J. A.), Yale University, New Haven, CT, 1985, Appendix 2.

(10) (a) Recently, Zuev and Sheridan[10b] have shown that *m*-phenylenebis(chloromethylene) is a singlet biscarbene. The construction of a conducting polymer based on this interesting compound presumably would require additional structural features not present in the biscarbene moiety itself, since the attachment of further such units at the *m*-phenylene positions is precluded. (b) Zuev, P. S.; Sheridan, R. S. *J. Org. Chem.* **1994**, *59*, 2267.