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Communications to the Editor

3,4-Dimethylenefuran and 3,4-Dimethylenethiophene, Heterocyclic Analogues of the Disjoint Non-Kekulé Hydrocarbon Tetramethyleneethane

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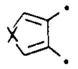
The title compounds, **1a** and **1b**, are π-conjugated non-Kekulé molecules[3] for which no full-valence structure can be written without expansion of the heteroatom octet (see **2a** and **2b**[4]). These species and their aza analogue **1c** have been invoked as reactive intermediates in the chemistry of the corresponding diallenyl systems **3**,[4-6] and **1a** is thought to be formed in the pyrolysis of 2,3-dimethylene-7-oxabicyclo[2.2.1]heptane.[7] Qualitative arguments as well as INDO/S-CI[8-10] and ab initio[9,11] calculations suggest that these biradicals should have singlet ground states, in violation of Hund's Rule. We now report new methods for the generation of **1a** and **1b** under circumstances that permit studies of their spectroscopic and chemical properties.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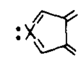
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3

a: X = O
b: X = S
c: X = NCH$_3$

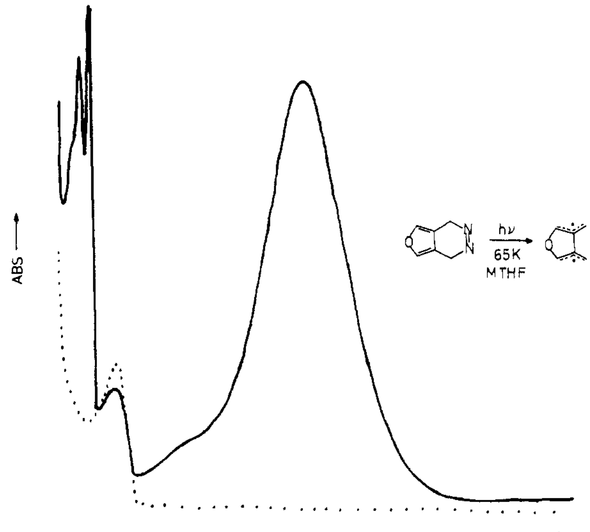
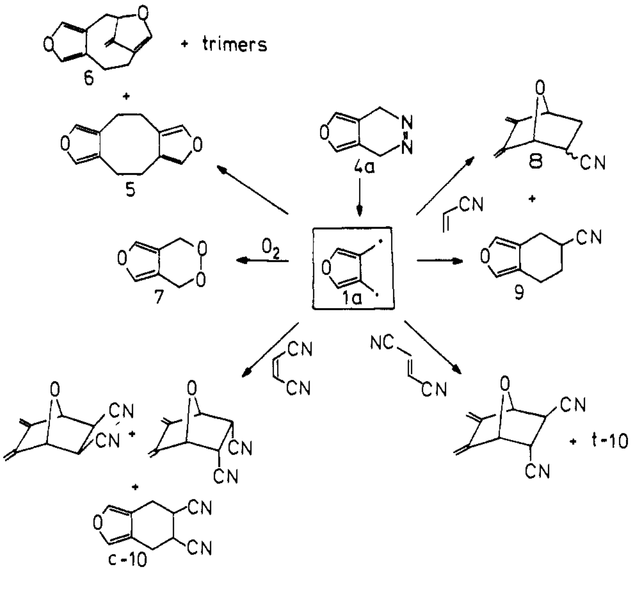


Figure 1. UV–vis spectra of **4a** before irradiation in MTHF glass at 65 K (···) and after 2 min of irradiation by filtered light ($310 < \lambda < 380$ nm) (—).

Scheme I



Diazenes 4a[12a] and **4b**[12b] were synthesized from 3,4-bis(chloromethyl)furan[12c,d] and 2,5-dibromo-3,4-bis(bromomethyl)thiophene,[12e] respectively. In solution, **4a** decomposes thermally (>0 °C) or photochemically (<−30 °C, 350-nm irradiation) to give a complex mixture of dimers and trimers $(C_6H_6O)_n$, where $n = 2$ or 3, empirically derived from the biradical **1a**. The two major products (40% yield)[13] are the known[6] dimer **5** and the new anti-Bredt dimer **6** (see Scheme I) formed in 2:1 ratio. Attempts to trap **1a** with simple alkenes or vinyl acetate were unsuccessful, but O_2 or acrylonitrile efficiently intercepts **1a** before dimerization can occur to give respectively the cyclic peroxide **7** (80%)[13] or a 64:24:12 mixture (at 25 °C) of bridged and fused adducts *endo*-**8**, *exo*-**8**, and **9** (70%).[13] In the thermal reaction, both the rate of disappearance of diazene **4a** and the ratio of acrylonitrile adducts are independent of the acrylonitrile concentration in the range 0.003–14 M and independent of the concentration of O_2. The same product ratio is observed in the photochemical reaction. The most economical interpretation of these results is that the rate-

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(1) American Cancer Society Postdoctoral Fellow, 1984.

(2) (a) Yale University. (b) University of Colorado. (c) National Institutes of Health Postdoctoral Fellow, 1984.

(3) For the coinage of the word "non-Kekulé", see: Dewar, M. J. S. *Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; p 233.

(4) (a) Garratt and co-workers have entertained the possibility that the thio analogue might be formulated as **2b**: Cheng, Y. S. P.; Dominguez, E.; Garratt, P. J.; Neoh, S. B. *Tetrahedron Lett.* **1978**, 6914. (b) See also: Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139. A dipolar carbonyl ylide contributing structure for **1a** can be written. Theoretical consideration of its significance is provided in the accompanying paper (ref 11).

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(12) (a) Compound **4a**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.31 (s, 2 H), 5.08 (s, 4 H); ^{13}C NMR (toluene-d_8, 248 K, 62.9 MHz) δ 135.34 (d), 112.50 (s), 55.97 (t); UV ($CHCl_3$) λ_{max} 363 nm, $\epsilon \sim 220$. (b) Compound **4b**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.14 (s, 2 H), 5.18 (s, 4 H); UV ($CHCl_3$) λ_{max} 362 nm, $\epsilon \sim 380$. (c) Novitskii, K. Yu.; Yur'ev, Yu. K.; Zhingareva, V. N.; Egorova, E. F. *Dokl. Akad. Nauk SSSR* (*Engl. Transl.*) **1963**, *148*, 856. (d) Rawson, D. I.; Carpenter, B. K.; Hoffman, H. M. R. *J. Am. Chem. Soc.* **1979**, *101*, 1786. (e) Zwanenburg, D. J.; Wynberg, H. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 321.

(13) Structures assigned by ^{1}H and ^{13}C NMR spectroscopy and elemental composition. Yields refer to isolated material based upon the two-step sequence from the hydrazine precursor of the diazene **4a**.

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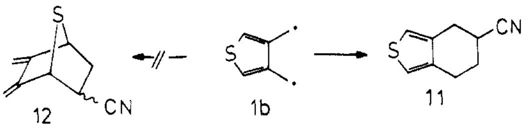
determining step in the thermal reaction is the unimolecular formation of a reactive intermediate **1a** and that only one spin state of **1a** is trapped.[14]

The trapping reaction with olefins is highly stereospecific (see Scheme I), which by reference to trimethylenemethane chemistry[15] is more readily interpreted in terms of the singlet rather than the triplet **1a** as the reactive species.

The generation and behavior of 3,4-dimethylenethiophene **1b** are analogous to those of **1a**, with one conspicuous exception: trapping of **1b** gives exclusively the *fused* thiophene derivative **11**, rather than the bridged isomer(s) **12**.



Photolysis ($310 < \lambda < 380$ nm) of a frozen glassy solution of **4a** in toluene, 2-methyltetrahydrofuran (MTHF), Et$_2$O, or EtOH at <80 K causes the rapid appearance of an intense purple color. The UV–vis absorption spectrum shows three new maxima at 338, 348, and 560 nm ($\epsilon > 10^3$) (Figure 1). Further irradiation at <80 K and then thawing of the glass cause the three bands to grow and diminish, respectively, at the same rate. Melting the matrix causes the color to vanish and ^{1}H NMR resonances characteristic of the dimers **5** and **6** to appear.[14] Similar phenomena are observed in the sulfur series, where the transient formed by photolysis of **4b** shows λ_{max} 572 nm ($\epsilon > 10^4$). In higher melting media (polycrystalline toluene for **4a**, Carbowax 400 for **4b**), the purple color of either transient is stable at 160 K. The transient from **4b** is not affected by irradiation at $\lambda > 420$ nm. We believe that the colored species from **4a** and **4b** are biradicals **1a** and **1b**, respectively.

Laser flash photolysis (355 nm) of a nitrogen-purged CDCl$_3$ solution of diazene **4a** at 10 °C gives rise within 25 ps to a transient, λ_{max} 560 nm, which is long-lived on the picosecond scale. When generated by a 351-nm 10-ns flash and monitored at 555 nm, the species has an apparent lifetime of about 3–4 μs in a nitrogen-purged solution. Whether this value is intrinsic to the biradical or merely measures the rate of capture by adventitious residual O$_2$ cannot yet be stated confidently. That the transient (or a species rapidly derived from it) reacts readily with O$_2$ is apparent from the time-dependent decrease in intensity of the 560-nm band (~20% after 50 ns, ~60% after 125 ns) when it is generated by picosecond flashes in O$_2$-saturated solution.

Photolysis ($310 < \lambda < 380$ nm) of **4a** or **4b** in MTHF glass at 12–80 K in the microwave cavity of an EPR spectrometer (Varian E-9) generates an intense purple color but does not give rise to a detectable triplet signal, even after prolonged irradiation.[16]

Although assignments of the lowest energy spin states of **1a** and **1b** are still tentative, all of the present evidence is consistent with a singlet in each case. The apparent experimental confirmation of the predicted[8-11] violation of Hund's rule supports the practical value of both semiempirical INDO/S-CI[8,9] and ab initio[10,11] quantum-mechanical calculations in guiding the search for non-Kekulé molecules with low-spin ground states.

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(14) (a) 3,4-Cyclobutafuran, the ring-closure product of **1a**, is a known compound.[7,14b] Control experiments now show that it does not react with acrylonitrile in CDCl$_3$ solution at 25 °C and is not formed in the solution or solid-phase reactions of **4a**. Flash vacuum pyrolysis of **4a** gives about 5% of the cyclobutane. (b) Vollhardt, K. P. C.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1973**, 214.

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(16) By the previously reported method,[17] the zero-field splitting parameter $|D|/hc$ for triplet **1a** is calculated to be 0.0279 cm^{-1} (STO-3G ROHF $^3B_2$ MOs, geometry optimized at the 3-21G UHF level). We thank Dr. Paul M. Lahti for this result.

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Quantitation of ^{2}H/^{1}H NMR Isotope Effects on ^{13}C Chemical Shifts. Linear Correlations Associated with Hybridization and Charge Density Changes in Norbornenyl Systems

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A common serious limitation to the study of compounds possessing distorted double bonds is a lack of crystallinity suitable for three-dimensional X-ray analysis. An extreme sensitivity to air oxidation[3] and/or dimerization[4] is also not easily accommodated. Our continuing interest in this class of molecules has led us to search for a new experimental method capable of determining *in solution phase* the extent of deformation at the olefinic center. As a first step toward this goal, we here report the discovery of both a hybridization and a charge density dependence to deuterium-induced ^{13}C NMR shifts for norbornene, norbornadiene, and structurally related molecules.

Günther et al. recently disclosed that one-bond ^{2}H isotope effects on the chemical shifts of carbon atoms in monodeuteriated ethane, ethylene, and acetylene vary linearly with the s character of the carbon atoms involved.[5] To our mind, the significance of this find would be appreciably enhanced if similar relationships could be shown to hold at positions of increasing distance from the isotopic label. We therefore chose initially to examine **1**–**3**, systems which share in common the rigid norbornane framework. Importantly, this series also offers a gradual progression in the hybridization at C5/C6, as determined by $^1J_{(C-H)}$ measurements.

Norbornene-2-*d* was prepared by Shapiro degradation of norbornanone (phenylsulfonyl)hydrazone and quenching of the intermediate vinyl anion with methanol-*d*.[6] To gain access to tricycle **2**, norbornenone ethylene ketal was cyclopropanated, deprotected, and subjected to a comparable Shapiro procedure.[7] Norbornadiene-*2-d* (**3**)[8] was made available by the method of De Lucchi et al.[9] using monodeuteriated (*Z*)-bis(phenylsulfonyl)ethylene (**6**)[10] as dienophile. For reasons to be discussed subsequently, the deltacyclene **4** and benzonorbornadiene **5** were also synthesized. Whereas **4** was obtained by extending the use of **6** to a Diels–Alder reaction with norbornadiene,[9] followed by sodium

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(1) Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985–1986.

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