Long-Lived Spin Isomerism of Singlet and Triplet States of *N*-Arenesulfonyl-3,4-dimethylenepyrroles

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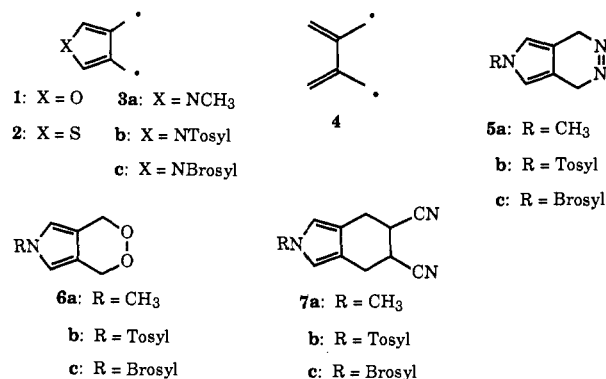*Department of Chemistry, Yale University*
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In the heterocyclic series of singlet biradicals **1–3**[1,2] derived conceptually from the disjoint biradical tetramethyleneethane (TME, **4**), the first-order perturbative interaction[1,3] between the heteroatom lone-pair orbital and the C_s symmetric TME NBMO, and hence the energetic preference for the singlet, should increase in the order O or S < NH (Chart I). However, this interaction should be sensitive to the electron-releasing (ER) or electron-withdrawing (EW) nature of a substituent on the nitrogen. A sufficiently EW group should result in a triplet–singlet gap E_T–E_S similar to those in hydrocarbon TMEs, which theory predicts[4] to be in the range –1 to +2 kcal/mol. Since the hydrocarbons, TME itself (**4**),[5a] 2,3-dimethylenecyclohexadiene (DMCH),[5b] and 5,5-dimethyl-2,3-dimethylenecyclopenta-1,4-diene (DMCP)[6] have been shown experimentally to have accessible and persistent triplet states, we proposed that the electronic tunability inherent in the pyrrole structure **3** might be used to populate a triplet state of the heterocycle. Semiempirical AM1-CI calculations[7] confirm the qualitatively predicted narrowing of the S–T gap with increasing EW nature of the substituent. This paper reports experimental tests of these predictions. It describes the preparation of the model substance **3a**, which has an ER substituent on N, and of two molecules **3b** and **3c**, each with a strong EW group on N. Compound **3a** persists as a singlet, but compounds **3b** and **3c** persist in *both* singlet and triplet states, which can be observed independently as kinetically stable species. The latter compounds demonstrate the rare phenomenon of *long-lived spin isomerism*.

By using procedures described elsewhere,[7] we have prepared the diazenes **5a–c**, potential precursors to the biradicals **3a–c**, respectively. Compound **5a** is thermally stable only at temperatures below –20 °C. Irradiation of a 2-methyltetrahydrofuran (MTHF) glass at 77 K at 365 nm or with the full spectrum (infrared-blocked) of a 200-W Hg arc gives rise to a blue, ESR-silent preparation of **3a**, λ_{max} 600 nm. The biradical **3a** putatively generated from **5a** in solution-phase preparative scale reactions by thermolysis or by photolysis at 365 nm gives dimers and interception products (*e.g.*, **6a** from O$_2$) and alkenes (*e.g.*, **7a** from fumaronitrile) analogous to those observed[1,2] with the furan and thiophene singlet biradicals **1** and **2**. Nanosecond time-resolved spectroscopy[8] directly confirms the quenching of **3a** by these trapping agents.

In contrast to **5a**, diazenes **5b** and **5c** are less reactive and persist for a few minutes even at room temperature. The photochemistry of MTHF or ether–isooctane–ethanol (EIA) glasses of these materials at 77 K is exquisitely sensitive to the

Chart I

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(2) Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3671 and references cited therein.

(3) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 8086.

(4) (a) Du, P.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 930. (b) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4743. (c) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 270.

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(6) Roth, W. R.; Kowalczik, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1285.

(7) Supplementary material to this paper.

(8) Heath, R. B.; Bush, L. C.; Feng, X.-W.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.*, in press.

irradiating wavelength. The toluenesulfonyl derivative **5b** (λ_{max} 305, 343, and 370 nm) irradiated at 370 nm (1000-W Hg–Xe arc, Oriel monochromator) rapidly gives a blue preparation, λ_{max} 593 nm, $\epsilon \sim 5100$, which is ESR-silent between 10 and 77 K. We assign the structure of singlet biradical **3b** to the carrier of the blue color. Although the color can be bleached photochemically and disappears quickly in thawed matrices, it persists in the dark at 77 K for at least 1 month. After this time, the samples still do not show any detectable ESR triplet signal. The *p*-bromobenzenesulfonyl derivative also gives an ESR-silent, blue preparation containing singlet **3c**, λ_{max} 600 nm, under the matrix immobilized conditions.

The same color appears when glasses containing both **5b** and a trapping agent, *e.g.*, maleonitrile or fumaronitrile, are irradiated as above. Annealing the glassy preparations gives trapping products **7b** resulting from completely stereospecific syn addition, as monitored by high-performance liquid chromatography (HPLC). The same products are obtained from liquid solution preparative runs in which **5b** and the trapping alkene are irradiated at –30 °C in CDCl$_2$ solution and the conversion is monitored by ^{1}H NMR at –40 °C. Product yields in the solution runs are near 100% by NMR and ~85% by actual isolation. Nanosecond spectroscopy[8] shows that the ratios of rates of quenching of the blue species **3b** by alkene trapping agents are the same as those determined in preparative competition experiments.

At 265 nm, 30–60-s irradiation of 0.005–0.01 M **5b** glasses at 77 K in MTHF or EIA gives a yellow preparation, $\lambda_{max} < 400$ nm, which displays (Figure 1) a strong triplet ESR spectrum.[9] The $\Delta m_s = 1$ transitions appear as a four-line signal centered around 3300 G at 9.281 GHz (superimposed on a weak doublet impurity peak). A weaker $\Delta m_s = 2$ line appears near 1650 G. The ESR spectrum can be simulated with the zero-field splitting parameters $|D/hc| = 0.0226$ cm^{-1} and $|E/hc| \leq 0.0005$ cm^{-1}. The value of $|D/hc|$ is very close to those of the three known TME triplet species: TME[5a] 0.025, DMCH[5b] 0.024, and DMCP[6] 0.026 cm^{-1}. Using PM3 wave functions[10] in a point-dipole procedure previously described,[11] we calculated the $|D/hc|$ values expected for both the TME and **3b** triplets to be 0.024 and 0.026 cm^{-1}. We assign the structure *N*-(*p*-toluenesulfonyl)-3,4-dimethylenepyrrole (**3b**) to the carrier of this triplet spectrum. Similar results are obtained from the bromobenzenesulfonyl derivative **5c**, which gives the triplet biradical **3c**, $|D/hc| = 0.0231$ cm^{-1} and $|E/hc| \leq 0.0005$ cm^{-1}. The ESR signal of **3b** persists in the dark at 77 K for at least 1 month. Both triplet preparations **3b** and **3c** show

(9) (a) The actual conversion under these conditions is <5%, as monitored by low-temperature, solution-phase NMR of recovered irradiated samples, and ~2% by direct ESR spin count. It is not clear that the observed color is attributable to the carrier of the ESR signal. (b) Irradiation of **5b** at 343 nm gives a different ESR triplet signal which has a smaller zero-field splitting, $|D/hc| = 0.014$ cm^{-1}.

(10) (a) Stewart, J. P. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. P. P. *J. Comput. Chem.* **1989**, *10*, 221.

(11) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.

Communications to the Editor

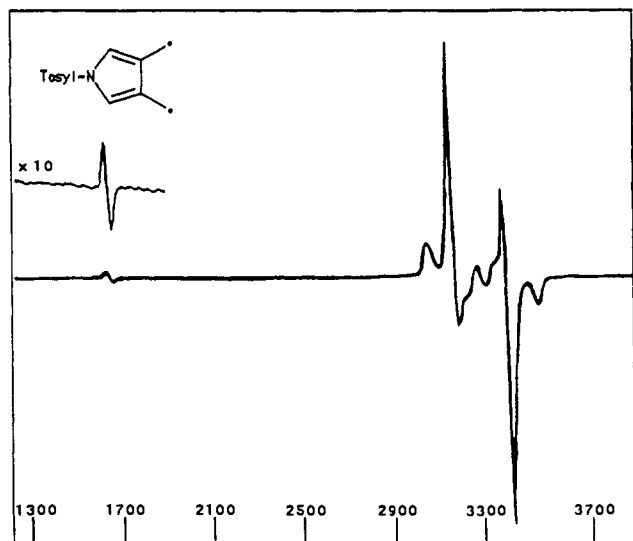*J. Am. Chem. Soc., Vol. 115, No. 21, 1993* 9831

Figure 1. Electron spin resonance spectrum observed after a 5-minute irradiation of a MTHF glass containing 0.009 M diazene **5b** at 265 nm and 77 K.

linear Curie law plots (ESR signal intensity *vs* $1/T$) in the range 12–40 K (temperatures nominal), but the signals lose intensity irreversibly at higher temperatures.

Even in EIA–heavy-atom solvent mixtures containing 1-bromopropane, iodoethane, or xenon at 77 K, interconversion of the ESR-silent blue species **3b** and **3c** with their triplet spin isomers does not occur over a period of days. We have considered two explanations for this phenomenon. The first recognizes that a disjoint singlet biradical would have almost purely covalent wave functions for the two electrons in the nominally nonbonding HOMOs.[12] As Salem and Rowland have shown,[13] unless the singlet wave function has appreciable ionic character, the spin-orbit matrix elements that couple the triplet and singlet would

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

approach zero, and slow intersystem crossing (isc) would be predicted. Just how slow such isc processes may be is still unclear.[14]

Alternatively, we suggest that because of the near-zero singlet–triplet energy gap, minor energetic factors such as the molecular conformation of the biradical might determine the spin of the ground state. In the rigid matrix, these conformations would be fixed at birth by the conformations of the precursor. Since interconversion of the biradical conformers would be matrix-impeded, spin interconversion might be immeasurably slow.

Curie law studies exemplify a class of experiments that purport to determine the spin of the thermodynamically preferred state of a biradical by observation of magnetic properties. It is a crucial (but infrequently stated[15]) assumption in such studies that the spin isomers achieve equilibrium rapidly. By demonstrating that this assumption is unreliable in some cases, the present results call for prudence in such assignments.

Supplementary Material Available: Descriptions of the syntheses and characterizations of new substances, spectroscopic methods, analyses of products, and quantum mechanical computations (23 pages). Ordering information is given on any current masthead page.

(13) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. See also: (b) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State;*Prentice-Hall, Englewood Cliffs, NJ, 1969; p 183. (c) Turro, N. J. *Modern Molecular Photochemistry;* Benjamin/Cummings: New York, 1978; Chapter 6. (d) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry;* Wiley-Interscience: New York, 1990; p 198.

(14) The 5% ionic character calculated[12] for the singlet of tetramethyleneethane (**4**) would suffice to permit isc at a rate many orders of magnitude faster than is observed for **3b,c**. Although it is just possible that a small perturbation by the nitrogen and its substituent could reduce the ionic character, and hence the rate, to near zero, the probability that this could occur with *both* **3b** and **3c** seems remote. We thank Professors L. Salem and W. T. Borden for helpful discussions of this point.

(15) See: Berson, J. A. in *The Chemistry of the Quinonoid Compounds;* Patai, S., Rappoport, Z., Eds., Wiley: New York, 1988; Vol. II, p 482 ff.