

# A New Class of Non-Kekulé Molecules with Tunable Singlet–Triplet Energy Spacings

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Received January 8, 1997

## Introduction

$\pi$ -conjugated non-Kekulé<sup>1</sup> molecules cannot be assigned classical structures<sup>2</sup> since they lack at least one bond from the number predicted by the standard rules of valence. Such units might serve as building blocks for the construction of polymers with useful ferromagnetic or electrically conductive properties, but a vast and largely unmapped terrain still must be explored before these practical objectives can be reached. Not only are we deficient in knowledge about the spin interactions among very weakly bound electrons within individual non-Kekulé molecules, but also we need to understand more about the specifically solid state intermolecular interactions between chains, which can be decisive in the ultimate bulk ferromagnetism or conductivity of a polymer.<sup>3</sup> Nevertheless, many laboratories already have made strides toward the actual synthesis of organic ferromagnets by ligation of non-Kekulé units.<sup>4</sup> Our own group has concentrated on the non-Kekulé molecules themselves, whose very existence as kinetically stable species evokes fundamental questions about the interrelationships among molecular structure, spin, and reactivity. Although our objective is primarily to answer such questions, we believe that the knowledge so gained is likely to find significant practical applications.

We have now designed and synthesized a new series of non-Kekulé molecules in which it is experimentally possible to adjust the energy separation of the frontier orbitals of the singlet state, as well as the actual singlet–triplet energy gap, gradually and at will.<sup>5,6</sup> This tuning offers the means to reduce the singlet–triplet gap to near zero, and thereby to gain the power of choice over the total electron spin of the molecule. In the creation and exploration of a domain of chemistry in which two “ground state” multiplets of the same molecular connectivity exist within a narrow energy range, we expected the unexpected, and we found it.

## The Parent System and the Perturbing Structural Feature

The necessary elements of this approach are a parent system with near-degenerate multiplet states, a variable

structural feature that can be used to perturb their separation, and a theoretical means for selecting potentially fruitful structural alterations. Our starting structure was the hydrocarbon biradical tetramethyleneethane (TME, 1). Superficially, this might seem a misguided choice, because although the molecule had been prepared and assigned a triplet ground state,<sup>7</sup> the size of the energy separation between the lowest multiplet states of TME was not (and is not) yet known from experiment. Nevertheless, we felt confident that the gap in TME, a *disjoint* species,<sup>8</sup> should be small. In fact, high-level *ab initio* theory<sup>9</sup> predicted a very small gap ( $E_T - E_S \approx +2$  to  $-1$  kcal/mol). This provided the first element in our tuning process. The second, a variable source of electronic perturbation, we introduced by a heteroatom bridge connecting two termini of the TME molecule, as in 3,4-

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Jerome A. Berson has taught at the University of Southern California (1950–1963), the University of Wisconsin (1963–1969), and since 1969, at Yale University, where he is now Sterling Professor Emeritus of Chemistry. His research group has studied the mechanisms of organic reactions and has synthesized molecules designed to stimulate theoretical investigation.

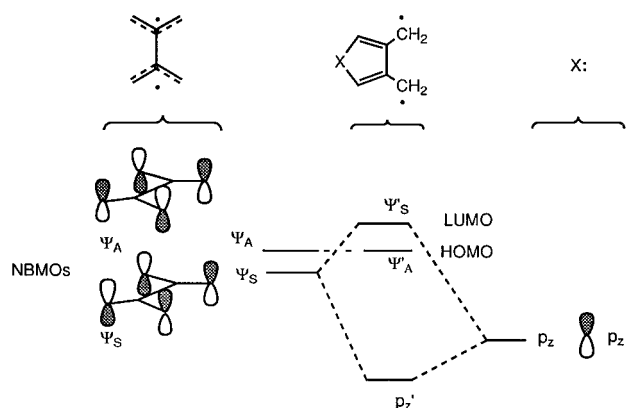
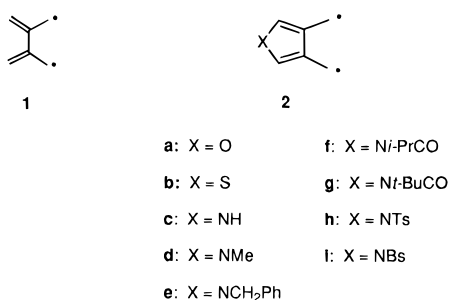


FIGURE 1. Perturbative interaction of the filled heteroatomic  $p$ - $\pi$ -orbital with the NBMOs of TME.<sup>10</sup> Reprinted with permission from ref 6b. Copyright 1997 American Chemical Society.

dimethylenefuran (**2a**), 3,4-dimethylenethiophene (**2b**), and the 3,4-dimethylenepyrroles (**2c–i**).



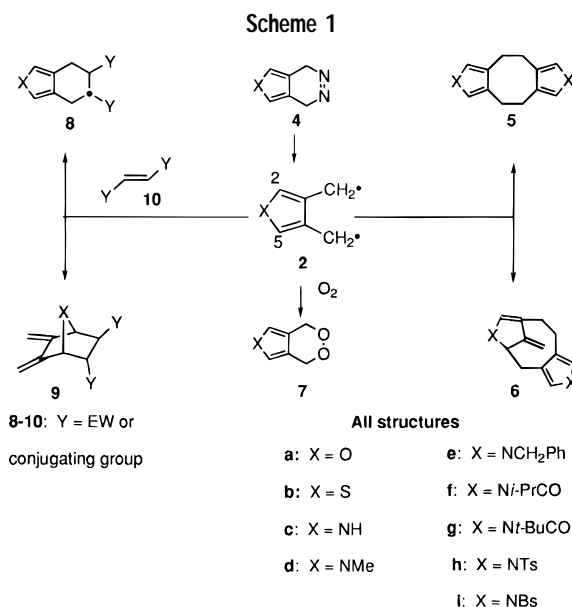
The remaining element, a computational protocol, emerged from qualitative but graphic arguments first explicitly made in connection with *ab initio* theoretical calculations by Du, Hrovat, and Borden;<sup>10</sup> the orbital relationships also can be derived from the results of semiempirical studies.<sup>5d–f</sup> Figure 1, a diagrammatic display of the idea, shows the effect of a heteroatom on the nominally nonbonding frontier  $\pi$ -orbitals (NBMOs) of the hydrocarbon TME (**1**). Because of a stabilizing through-space interaction, the unperturbed orbital  $\Psi_S$  of hydrocarbon **1** is lower in energy than  $\Psi_A$ . By symmetry, the lone-pair orbital  $p_z$  perturbs  $\Psi_S$  but not  $\Psi_A$ . Thus, in the 3,4-dimethyleneheterocycles, e.g., **2a,b** and **2c–i**, the relative energies of the original TME NBMOs ( $\Psi_A$ ,  $\Psi_S$ ) are perturbed by an amount that, to first order, will be inversely proportional to the energy separation between one of them and the lone-pair  $p_z$  orbital.<sup>11</sup>

At this point, it becomes clear that the effect of the heteroatom lone pair can either increase or decrease the energy gap between  $\Psi_S$  and  $\Psi_A$ . If the  $\Psi_S$ -lone-pair interaction is weak, it could bring  $\Psi_S$  and  $\Psi_A$  closer together than they are in TME itself, thereby tending to favor a triplet ground state, but if strong, it could drive  $\Psi_S$  higher than  $\Psi_A$ , inverting the order of the FMOs; if strong enough, it would favor a singlet. The MO calculations (Table 1) show that in the lowest singlet states of both the furan and thiophene heterocyclic derivatives **2a**

**Table 1.** Energy Separations of Lowest Singlet and Triplet States of non-Kekulé Compounds Calculated by Semiempirical and *ab Initio* Methods

Compound	$E_T - E_S$ (calc.), kcal/mol <sup>a</sup>		
	INDO/S-CI <sup>b</sup>	AM1/CI <sup>c</sup>	SVP, SD- $\pi$ -CI <sup>d</sup>
<b>1</b>	0.5	1.5	1.7
<b>2a</b>	0.5, 0.6	4.8	2.3
<b>2b</b>	0.4	4.8	<i>e</i>
<b>2c</b>	4.3	9.8	6.8

<sup>a</sup> See ref 5b and references cited therein. <sup>b</sup> Reference 5d. <sup>c</sup> Reference 5e. <sup>d</sup> Reference 10. <sup>e</sup> Not calculated.



and **2b**, the perturbation is strong. Orbital  $\Psi_S$  is in fact higher than  $\Psi_A$ , and the singlet is predicted to be the ground state (Table 1). These predictions for **2a** and **2b** are confirmed experimentally.<sup>5</sup>

In the case of the parent pyrrole TME derivative **2c**, the heteroatom unit is NH, a strong electron donor, and the calculations confirm the qualitative expectation that the perturbation should be even stronger than in the furan and thiophene systems. As we shall see, the functional NH group in the pyrrole offers a special opportunity to adjust the electronic nature of the heteroatom and hence to *tune* the singlet–triplet gap by replacement of H with electron-withdrawing or electron-releasing groups (EWG or ERG).

## Chemistry and Reactivity of the Singlets.<sup>5a–d,6b</sup> Direct Observation of the Purple and Blue Biradicals

The immediate synthetic precursors of these biradicals are the corresponding diazenes **4** (Scheme 1), which can be deazetated thermally or photochemically. We defer a

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

(11) Differences in overlap also will affect the perturbation but are not explicitly treated in the diagram of Figure 1. This influence of course is present implicitly in the parametrization schemes of the various semiempirical computational approaches we have used.

discussion of the arenensulfonyl derivatives **2h** and **2i**, but the singlet biradicals **2a–g** can be observed directly, when generated photochemically in a matrix-immobilized state, by their intense visible color and UV–vis absorption (purple,  $\lambda_{\text{max}} \approx 560$  nm,  $\epsilon \approx 5000$  for **2a** and **2b**; blue,  $\lambda_{\text{max}} \approx 600$  nm,  $\epsilon \approx 5000$  for **2d–g**). These preparations show no ESR signal such as could be attributed to a triplet, and the solution phase chemistry (see below) also points to a singlet spin state for these species.

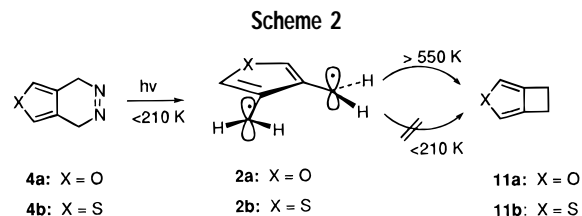
The absence of an ESR signal, as a negative experiment, of course does not prove that the biradicals are singlets. In principle, NMR spectroscopy could provide a more direct demonstration of singlet character. The unpaired electron spins of a triplet would contact-shift the transitions by thousands of parts per million and broaden them by thousands of hertz. Thus, only a singlet species should show unbroadened lines at normal chemical shifts, and the triplet should not be observable under ordinary conditions. Zilm and his co-workers<sup>51–n</sup> have developed methods for the low-temperature solid state cross polarization magic angle spinning (CP MAS) <sup>13</sup>C NMR spectroscopy of isotopically enriched preparations of the biradicals. The observations<sup>51–n</sup> of unbroadened <sup>13</sup>C resonances in immobilized specimens of **2a**-*di*-<sup>13</sup>CH<sub>2</sub> at 102 ppm, in **2b**-*di*-<sup>13</sup>CH<sub>2</sub> at 105 ppm, and in **2b**-2,5-*di*-<sup>13</sup>CH at 115 ppm, produced by irradiation of matrices of the corresponding isotopically enriched diazenes, are strong evidence of the singlet character of these biradicals. The intensities of the UV–vis spectra of **2a** and **2b** are well-correlated with those of the NMR signals, which indicates that the two techniques measure a common species.

When fumaronitrile (**10**) (Y = CN), a reactive alkenic trapping agent, is incorporated into the matrix containing **2b**-*di*-<sup>13</sup>CH<sub>2</sub>, and the preparation is annealed to 120 K, a temperature at which the diazene is thermally stable, the intensity of the 105 ppm resonance of **2b**-*di*-<sup>13</sup>CH<sub>2</sub> diminishes and is replaced quantitatively by that of a new resonance at 28 ppm associated with the  $\alpha$ -carbons of the adduct **8**-*di*-<sup>13</sup>CH<sub>2</sub>. This establishes the singlet biradical as the reactive entity in cycloaddition.

### Unimolecular Chemistry of **2a** and **2b**

In poly(methyl methacrylate) or other transparent films, the UV–vis spectrum of the thiophene biradical **2b**, for example, can be observed up to the softening point of the film (>210 K).<sup>5d</sup> At higher temperatures, the spectrum fades, presumably because the biradicals are then able to diffuse together and dimerize (see below). The threshold temperature for *unimolecular* thermal reaction may be much higher, since, in some cases, the purple color can be seen in harder matrices such as poly(tetrafluoroethylene) even at room temperature. It is possible to surmount the threshold at higher temperatures by flash vacuum pyrolysis of the appropriate diazene **4a** or **4b** at >550 K, which produces the cyclobutaheterocycle **11a** or **11b**, respectively (Scheme 2).<sup>5d</sup>

Since dimerizations of simple alkyl radicals occur at nearly every encounter,<sup>12</sup> it seems at first glance incredible



that two spin-paired radical sites in close proximity, as in **2a** and **2b**, should resist immediate combination, even at low temperature, to the cyclobutaheterocycle **11a** or **11b**. The retardation in rate probably results from strain and from the need to twist the exocyclic methylene groups out of the plane of the heterocyclic ring en route to the transition state for ring closure, which would cost some of the 20 kcal/mol of stabilization associated with two allylic systems in the biradical **2a** or **2b**.

### Intermolecular Reactions of the Singlet Biradicals

In solution, the biradicals formed in the decompositions of the diazenes dimerize to the symmetrical (**5**) and unsymmetrical (**6**) structures (see Scheme 1). The rates of these dimerizations,<sup>5h–j</sup> measured by nanosecond time-resolved methods, are essentially at the diffusion-limited value ( $\sim 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  under these conditions<sup>12</sup>). In the combination of two singlets, every encounter pair is spin-allowed to form product, and these biradical dimerizations must be among the fastest bimolecular reactions known.

The biradicals **2a–g**, when generated in solutions containing olefinic trapping agents (**10**) or dioxygen, can be intercepted in high yield as 1:1 adducts **8–9** or **7**, respectively.<sup>5a–j,6b</sup> The mechanism of the thermally initiated cycloaddition in several cases has been established by kinetic means to proceed by two successive steps, namely, unimolecular deazetation to give the biradical reactive intermediate **2**, followed by bimolecular capture of the biradical.<sup>5b,c,6b,c</sup> The reactions of the biradicals with stereochemically defined alkenes are stereospecific for *syn*-addition: *cis*-alkenes give *cis* adducts, and *trans*-alkenes give *trans* adducts, exclusively (>99%). This is consistent with the behavior expected of singlet biradicals.<sup>13</sup>

### Reactivity of the Singlet Biradicals in Cycloaddition. Structure of the Reactive Intermediate

The relative reactivities of the biradicals with a series of alkenic trapping agents in fluid solution can be determined by classical preparative pairwise competition experiments. Alternatively, the characteristic UV–vis absorption of the biradicals can be generated by nanosecond flash photolysis in such media, and the rates of quenching by alkenes can be measured directly with nanosecond time resolution. The relative rates determined by the two

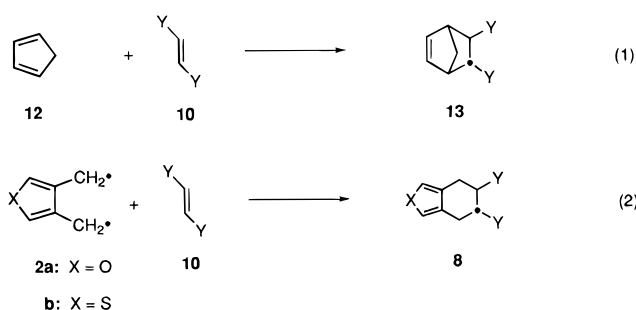
(12) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1 and references cited therein.

(13) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4 and references cited therein.

methods agree within experimental error,<sup>5a,c,g-j</sup> which again shows that the carrier of the purple or blue color and the UV-vis spectrum is not just a side product of unknown structure but in fact is the same reactive intermediate as that responsible for the preparative chemistry.

### Diyls as "Superdienes" in Cycloaddition. Breakdown of the Reactivity-Selectivity Relationship

There was early evidence,<sup>5b</sup> subsequently repeatedly confirmed,<sup>5g-j</sup> that the reactivity sequences of alkenes **10** in Diels-Alder additions to conjugated dienes such as 1,3-cyclopentadiene (**12**) (eq 1) ran parallel to those in cycloaddition to the 3,4-dimethyleneheterocycles **2a** and **2b** (eq 2).



The relative reactivities in diene additions (eq 1) of the alkenes maleic anhydride, fumaronitrile, dimethyl fumarate, and acrylonitrile cover a range of ~5000-fold.<sup>14a</sup> Surprisingly, the orders and relative magnitudes of the rates of the diene additions of eq 1 and the diyl additions of eq 2 with the same alkenes are essentially the same.<sup>5g-j</sup> This discriminatory ability of the series of alkenes persists even though the diyl reactions of eq 2 are some 10<sup>10</sup> times as fast as the diene reactions of eq 1. Superficially, one might have expected the so-called "reactivity-selectivity relationship"<sup>15</sup> to produce a much narrower range of reactivities in the more reactive diyl series.

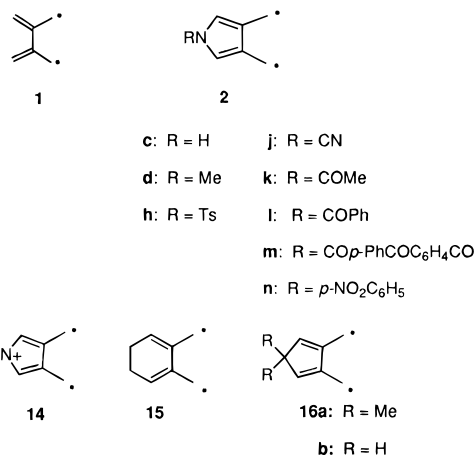
There is another initially puzzling aspect of the data: the absolute and relative rates of the diyl reactions (eq 2) have little or no temperature dependence.<sup>5j</sup> Thus,  $\Delta H^\ddagger$  and  $\Delta\Delta H^\ddagger \approx 0$ , and the reactivity range is controlled entirely by variations in  $T\Delta S^\ddagger$ ; on the other hand, in the diene reactions (eq 1),<sup>14a,b</sup>  $T\Delta\Delta S^\ddagger$  is essentially zero throughout the series, and the reactivity range is controlled entirely by  $\Delta\Delta H^\ddagger$ . Nevertheless, not only do the reactivities of the diyl and diene reactions correlate with each other, but also *both* correlate with the frontier MO (FMO) energy separation.<sup>5g-j</sup> This suggests that the fa-

miliar Eyring activation energy and activation entropy terms have a common physical basis.<sup>5j,16</sup>

### Tuning the Singlet-Triplet Energy Gap in the N-Substituted 3,4-Dimethylenepyrrole Series

Replacement of the functional hydrogen of the NH group in the pyrrole series by an EWG would lower the energy of the lone-pair  $p_z$  orbital in Figure 1 and thereby attenuate the perturbation of the symmetric component of the TME NBMOs. A sufficiently EW substituent should result in a triplet-singlet gap similar to those in hydrocarbon TMEs. In the extreme, it should be possible to switch off the interaction of the TME NBMO and the nitrogen lone pair by N-protonation of **2c**, as in the pyrrolium ion **14**.

Experimentally, three examples of hydrocarbons of the TME series have been shown to have thermally accessible and persistent triplet states: TME (**1**) itself<sup>7</sup> and two derivatives, 2,3-dimethylenecyclohexa-1,3-diene (**15**)<sup>17</sup> and 5,5-dimethyl-2,3-dimethylenecyclopenta-1,3-diene (**16a**).<sup>18</sup>



### AM1/CI Calculations

Figure 2<sup>6a,c</sup> provides computational confirmation of the qualitative perturbational ideas. As expected, in the N-protonated pyrrolium species **14**, the  $E_T - E_S$  gap is calculated to be essentially the same as in the TME hydrocarbons **1** and **16b**. In the pyrrole series **2c-n** (Figure 2), the LUMO coefficient on nitrogen, plotted as the abscissa, measures the mixing of the nitrogen lone-pair orbital with the TME NBMOs (see Figure 1). One set of calculations predicts the gap  $E_T - E_S$  (relative to that for TME, **1**) for the "vertical" separation of the multiplet states when both multiplets are assumed to have the geometry optimized for the more stable of the two; another set gives values of the gap for the states with the geometries individually optimized. The results do not differ significantly for the present purposes. As expected, the mixing decreases as the N-substituent becomes more

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(15) See: Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 162 ff.

(16) (a) Reference 5j explains this with a curve-crossing model derived as a corollary of Houk's model<sup>16b</sup> of entropy-controlled reactions. (b) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555 and references cited therein.  
(17) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1987**, *109*, 5284.  
(18) Roth, W. R.; Kowalczyk, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Müller, W. *Angew. Chem., Intl. Ed. Engl.* **1987**, *26*, 1285.

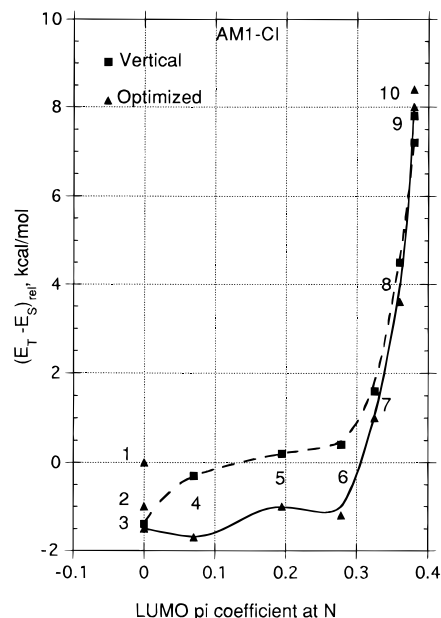


FIGURE 2. Calculated vertical and optimized triplet-singlet energy separation (relative to that of TME (1) set as zero) as a function of the LUMO  $\pi$ -electron coefficient at N for a series of N-substituted 3,4-dimethylenepyrroles and other biradicals. The values were obtained with AM1, OPEN (4,4)/4CI. Points 1–3 represent compounds as follows: (1) TME (1); (2) 16b; (3) 3,4-dimethylenepyrrolium ion (14). These points should be read with reference only to the ordinate. Points 4–10 represent N-substituted 3,4-dimethylenepyrroles with substituents as follows: (4) *p*-nitrobenzoyl (2n); (5) *p*-benzoylbenzoyl (2m); (6) benzoyl (2l); (7) acetyl (2k); (8) cyano (2j); (9) methyl (2d); (10) hydrogen (2c). The curves are merely smooth connections of the points. Reprinted with permission from ref 6b. Copyright 1997 American Chemical Society.

electron-withdrawing, and ultimately, the multiplet separation approaches that of the TME hydrocarbons **1** and **16b**.

Both of the curves of Figure 2 decline to nearly flat plateaus in the region of  $(E_T - E_S)_{rel} \approx 0$  to  $-1$  kcal/mol. Thus, the main message to be read from Figure 2 is that an alkyl group (*cf.* methyl, point 9) or weakly EWG such as acyl (*cf.* COMe, point 7) should result in a singlet 3,4-dimethylenepyrrole, but EWG N-substituents as strong as *p*-nitrobenzoyl (point 4) or stronger should produce an accessible triplet state. For reasons given elsewhere,<sup>6</sup> we chose the *p*-toluenesulfonyl (tosyl,  $C_7H_7SO_2$ ) group as a strong EWG N-substituent in biradical **2h**, and as comparison molecules, we prepared other members of the pyrrole biradical series **2d–i** (Scheme 1).

### The Singlet States of *N*-Tosyl-3,4-dimethylenepyrrole (**2h**) and Other *N*-(Arylsulfonyl)-3,4-dimethylenepyrrole Derivatives<sup>6a,c</sup>

As we noted above, the *N*-alkyl (**2d**, **2e**) and *N*-acyl (**2f**, **2g**) pyrrole derivatives, when generated from their respective diazene precursors (see Scheme 1, **4d**, **4e** and **4f**, **4g**), behaved as singlet biradicals. We were now ready to test our idea of reversing the multiplicity to triplet by changing the N-substituent to a strong EWG. With pleasurable anticipation, we irradiated, at 370 nm and 77 K, a glassy sample of the *N*-tosyldiazene **4h**, the appropriate precursor of the biradical *N*-tosyl-3,4-dimethylenepyrrole (**2h**).

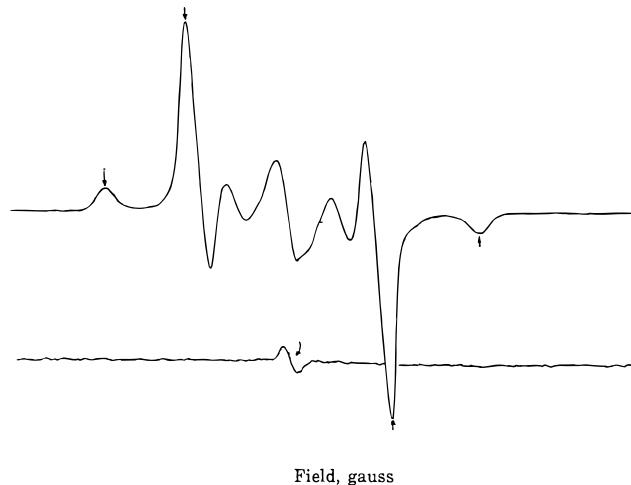


FIGURE 3. ESR spectrum obtained by 265 nm irradiation of *N*-tosyldiazene **4h** in ether-isopentane-ethanol glass at 77 K for 1.5 min. The spectrometer frequency is 9.296 GHz. The upper trace shows the  $\Delta m_s = 1$  region; the peaks of the spectrum associated with  $^3\mathbf{2h}$  are marked with arrows and occur at 3075, 3184, 3430, and 3558 G. The unlabeled peak in the middle of the spectrum and the two peaks flanking it are associated with side-reaction products formed in the photolysis.<sup>6a,c</sup> The lower trace is offset and shows the  $\Delta m_s = 2$  region centered at 1662 G. Reprinted with permission from ref 6c. Copyright 1997 American Chemical Society.

The sample quickly turned deep blue and showed a strong band in the UV-vis spectrum at 593 nm,  $\epsilon = 5000 \text{ M}^{-1} \text{ cm}^{-1}$ . This spectrum immediately caused dismay, since it was very similar to those observed for the *singlet* species **2a–g** (Scheme 1). The solution phase chemistry also was characteristic of a singlet. Trapping reactions with stereochemically labeled electron-deficient alkenes gave completely stereospecific cycloaddition products.

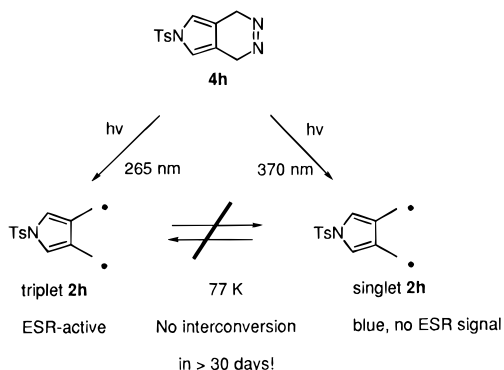
In these adducts, the structural elements of *N*-tosyl-3,4-dimethylenepyrrole (**2h**) are incorporated intact. Several lines of evidence point to the biradical **2h** itself as the carrier of the blue color and identify it as the actual reactive intermediate in the formation of the adducts.<sup>5h,6b</sup>

The singlet biradical **2h** was indefinitely stable in glassy matrices up to at least 200 K. No ESR signal attributable to a triplet species was seen in the samples between 10 and 90 K. Of course, these were disappointing results, since our carefully designed approach to populating an observable triplet state of **2h** apparently did not work. However, the frustration was only temporary, and we soon discovered how to make the triplet.

### The Triplet State of *N*-Tosyl-3,4-dimethylenepyrrole<sup>6a,c</sup>

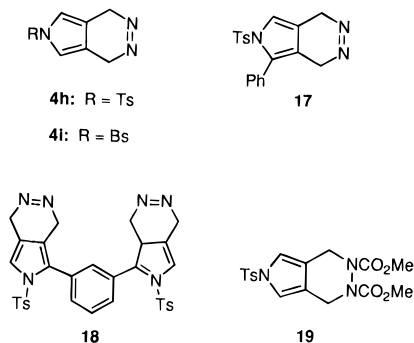
The previous photochemical deazetations of the diazene **4h** leading to the blue singlet biradical **2h** had been carried out using light of 370 nm, a wavelength that lies within the weak series of bands of the azo chromophore. However, monochromatic light of 265 nm or filtered light of 230–320 nm produced a very different result. The glassy matrix turned yellow, not blue; no UV-vis band near 600 nm was observed. ESR examination of such preparations showed the well-developed triplet spectrum shown as Figure 3, with the zero-field parameters  $|D|hc = 0.0226 \text{ cm}^{-1}$  and  $|E|hc \approx 0 \text{ cm}^{-1}$ . Note especially the

Scheme 3. Irradiations in Glassy Matrices



presence of the tell-tale  $\Delta m_s = 2$  resonance near half-field. The  $D$  value is close to those of the three known TME hydrocarbon derivatives **1**, **15**, and **16a** (0.025, 0.024, and 0.0259  $\text{cm}^{-1}$ , respectively) and to the value calculated by semiempirical methods (0.0256  $\text{cm}^{-1}$ ). The ESR spectrum persisted in the dark for weeks, during which time no trace of the blue singlet could be detected. Numerous efforts to effect the interconversion of the triplet and singlet species were unsuccessful. Both biradical preparations were stable in dark matrices for extended periods.

We also observed the same wavelength-dependent photochemical behavior in three other related diazenes: **4i**,<sup>6a,b</sup> **17**,<sup>6d,e</sup> and **18**.<sup>6d,e</sup> Irradiation of each of these precursors at 77 K gave by deazetation (*monodeazetation* in the case of **18**) a blue singlet biradical at 370 nm and a colorless or yellow triplet at 265 nm. Each biradical multiplet, even in the case of the bromo derivative **2i** generated from diazene **4i**, was stable with respect to intersystem crossing (isc).



These phenomena seem to have no precedent in the field of non-Kekulé molecules; in particular, no such behavior has been reported in the group of TME hydrocarbons **1**, **15**, and **16a**, where only the triplet has been observed as a persistent species. We worried, of course, that the slow isc between the singlet and the triplet in the pyrrole biradicals might have the trivial cause that the multiplets had entirely different molecular structures. After extensive study,<sup>6a,c</sup> however, we were able to intercept the transients associated with the carrier of the triplet ESR spectrum. The trapping reaction with dimethyl azodicarboxylate in thawed matrices gave the product **19**, which contains intact the same *N*-tosyl-3,4-dimethylenepyrrole unit that is present in the singlet biradical **2h**. Thus, the hypothesis of different structures for the multiplets was

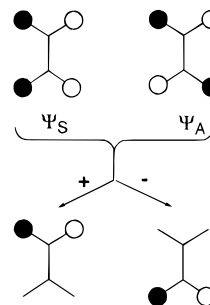


FIGURE 4. Disjoint orbitals of TME (**1**) by linear combination of the symmetry-adapted orbitals  $\Psi_S$  and  $\Psi_A$ .<sup>8</sup> Adapted from ref 8b.

untenable, and we were dealing with a true case of long-lived *spin isomers* (Scheme 3).

### Origins of the Long-Lived Spin Isomerism<sup>6a,c</sup>

The great majority of rate measurements for singlet–triplet isc pertain to transitions from electronically excited states either to other electronically excited states or to ground states that are much lower in energy. The known<sup>19</sup> values range over about 13 orders of magnitude, from  $10^{11}$  to  $10^{-2} \text{ s}^{-1}$ . Little is known about the rates of isc in systems where, as in the cases studied here, two multiplets are close competitors for the designation of “the ground state”. In the present *N*-(arenesulfonyl)-3,4-dimethylenepyrrole series, the isc rates are slower than that of the slowest known conventional “excited state” case by at least 5 orders of magnitude. We have considered two explanations for the unusually slow rates of isc.

The first is that biradicals of the TME type have *disjoint* NBMOs, in which, as Borden and Davidson have pointed out,<sup>8a,b</sup> the two frontier electrons can be confined to separate spatial domains (see Figure 4). In such circumstances, the singlet wave function of the biradical has little ionic character. Presumably, this also would apply in TME derivatives such as **2h**. Salem and Rowland<sup>20a,b</sup> have emphasized that spin–orbit-mediated isc should be slow in such molecules. But would it be slow enough to account for the startling separate persistence of the two forms of **2h**? As is explained elsewhere,<sup>6a,c</sup> the fractional ionic character would have to be no greater than  $10^{-8}$  in each of the four cases we have observed. This is inherently improbable, and the unanimous resistance to the idea by knowledgeable consultants<sup>20c</sup> persuaded us to look for a different interpretation.

We now suspect that although the persistent singlet and triplet forms of the *N*-(arenesulfonyl)-3,4-dimethylenepyrrole biradicals do have the same *connectivity*, they have *different conformations*, which are related by rotations around the N–S and S–arene ipso bonds of the biradical. There is computational evidence<sup>21</sup> that during a  $90^\circ$  N–S conformational change in the model 3,4-dimethylenepyrrole biradical *N*-substituted with the  $\text{HSO}_2$  group, the singlet–triplet energy gap changes by as much as 0.6–0.8 kcal/mol (Table 2). Quantum mechanical calculations<sup>22</sup> on model sulfonamides suggest rotational

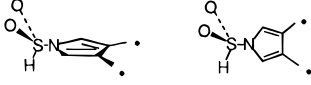
(19) A list of references is given in ref 6a,c.

(20) (a) Salem, L.; Rowland, C. *Angew. Chem., Intl. Ed. Engl.* **1972**, *11*, 92.

(b) See also: Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3568. (c) Salem, L.; Borden, W. T.; Davidson, E. Personal communications.

(21) Borden, W. T.; Hrovat, D. Personal communication, 1995.

**Table 2. Conformational Dependence of  $E_T - E_S$ , kcal/mol<sup>a</sup>**

ab initio method			$\Delta\Delta E$
	$E_T - E_S$	$E_T - E_S$	
CASSCF	5.3	5.9	0.6
CASPT2N/ 6-31G*	7.2	8.0	0.8

<sup>a</sup> Reference 21.

N–S barriers of 5–9 kcal/mol, which at the low temperatures of the matrix-immobilization experiments, would produce conformational lifetimes in the range of a few seconds to many centuries. Thus, in a **2h** biradical formed at low temperature in a particular conformation, and hence in a particular spin state, the multiplicity might be effectively frozen.

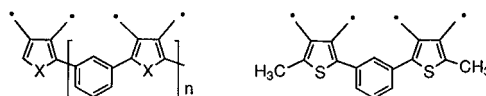
### Catenation of Non-Kekulé Biradicals to Tetraradical Prototypes of Conductive Polymers

In  $\pi$ -electron theory, each monomeric unit of the non-Kekulé series **2** embodies a pair of half-filled, nearly degenerate, nominally NBMOs. Catenation of singlet monomers such as **2a** and **2b** should lead to antiferromagnetic low-spin “nonclassical”<sup>23</sup> polymers **20a** and **20b**, in which the half-filled electron bands would confer the capability for metallic conduction<sup>3</sup> without doping. On the other hand, the triplet monomers, such as **2h** and **2i**, might lead to conductively insulating high-spin polymers of the type **20h** and **20i**, for example, with ferromagnetic properties.<sup>4</sup> In addition to the chains of type **20**, one could also imagine conducting or magnetic sheets in which an additional aryl heterocyclic unit initiates a branch at the *meta* position of the benzene ring of **20**.

(22) Breneman, C. M.; Weber, L. W. *Can. J. Chem.* **1996**, *74*, 1271. We thank Professor Breneman for an advance copy of this paper.

(23) Tyutyulkov, N.; Karabunarliev, S.; Ivanov, C. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 139 and references cited therein.

We have recently synthesized the first member of the potentially large family of catenated non-Kekulé molecules based upon this motif, the *m*-dithienylbenzene derivative **21**, a singlet tetraradical.<sup>6d,e</sup>



n is large

**20a**: X = O**20b**: X = S**20h**: X = NTs**20i**: X = NBs**21**

### Conclusions and Prospects

The present interpretation of the long-lived spin isomerism of the *N*-(arylsulfonyl)-3,4-dimethylenepyrrole derivatives implies that the singlet–triplet energy gap changes with conformation by a small but finite amount (computationally less than 1 kcal/mol). In order for this to switch the predominant multiplicity, as proposed for the present examples, the energy gap between the triplet and the singlet would have to be nearly zero, the relationship we sought to create at the outset.

Perhaps it is not totally fanciful to imagine the eventual practical application of such knowledge to molecularly based devices that exploit the reversible interconversion of a magnetic insulator and an electrical conductor. One obvious goal therefore is the construction of non-Kekulé molecules in which the rate of conformationally mediated isc becomes observable.

*I thank the co-workers whose names are given in the references for their valuable collaboration in these efforts. Professor W. T. Borden gave helpful advice on theoretical issues. The National Science Foundation, the American Chemical Society's Arthur Cope Scholar program, and the Dox Foundation gave financial support. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.*

AR9700015