

# Triplet Species from Dihydropyrrolo[3,4-*d*]pyridazines, the Diazene Precursors of *N*-Arenesulfonyl-3,4-dimethylenepyrroles

Linda C. Bush,<sup>†</sup> Ljiljana Maksimovic, Xu Wu Feng, Helen S. M. Lu, and Jerome A. Berson\*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

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**Abstract:** In contrast to the photolyses of *N*-methyl- or *N*-pivaloylpyrrolo[3,4]dihydropyridazines in low-temperature matrices, which give the blue, ESR-inactive singlet 3,4-dimethylenepyrrole biradical at all wavelengths, the photolyses of the *N*-arenesulfonyl derivatives in this series are strongly wavelength-dependent. In three separate instances, both singlet and triplet *N*-arenesulfonyl-3,4-dimethylenepyrrole biradicals have been observed. In each case, one or two other triplets are seen by ESR spectroscopy after irradiation under special conditions. These are tentatively assigned conformationally isomeric diazenyl biradical structures. The possible origins of the slow intersystem crossing rates for singlet–triplet interconversions in *N*-arenesulfonyl-3,4-dimethylenepyrrole biradicals are examined. Near-zero ionic character of the singlet wave function is considered to be a less likely cause than conformational control of the spin state. The latter circumstance would require that intersystem crossing be coupled to conformational change, which can be very slow at low temperatures. The zero-field splittings determined from the ESR spectra of *N*-tosyl-3,4-dimethylenepyrrole biradical are found to be temperature-dependent, which could be caused by librations and/or internal rotational (conformational) motions of the biradical in the matrix.

In recent work,<sup>1a,c–e</sup> we applied semiempirical quantum chemical calculations, calibrated on experimental observations and high-level ab initio computations, to develop guidelines for the construction of non-Kekulé molecules with near-zero singlet–triplet (S–T) energy gap. These studies led to the prediction that the preference for a singlet ground state characteristic of the parent 3,4-dimethylenepyrrole biradical **1a** should decrease as the hydrogen of the N–H function is replaced by increasingly electron-withdrawing (EW) groups. The *N*-methyl substituent and even the moderately EW *N*-pivaloyl substituent should still preserve the singlet ground state, in accord with the observed chemistry of the corresponding biradicals<sup>1</sup> and with the absence of ESR signals from matrix-immobilized samples generated at low temperatures. However, with an *N*-substituent as strongly EW as arenesulfonyl (as in **1b,c**), the T–S energy gap was anticipated to be very small<sup>1a,c</sup> and about the same as that predicted (+2 to –1 kcal/mol) by the most recent ab initio results<sup>2</sup> for hydrocarbon tetramethyleneethane (TME) derivatives. Three such hydrocarbon TMEs (**2–4**) have been shown experimentally to have accessible triplet states which have been characterized by electron spin resonance (ESR) spectroscopy.<sup>3</sup> Thus, there was legitimate reason to hope that the heterocyclic biradicals **1b,c** might have observable triplet states also.

On the other hand, the experimental evidence<sup>1</sup> so far leaves little doubt that the ESR-silent blue transient species of  $\lambda_{\max} =$

593 nm generated by thermolysis or direct 370 nm photolysis of diazene **5b** is a *singlet* state of *N*-tosyl-3,4-dimethylenepyrrole **1b**.<sup>1b,c</sup> This apparent failure of the computationally based predictions of an accessible triplet of **1b** was a sharp disappointment.

However, further study gradually revealed a complex set of photochemical pathways of the diazene **5b**. The photochemistry is exquisitely sensitive to the temperature and irradiating wavelength, and eventually, we were led to the discovery of *three* new triplet species, one of which has properties consistent with those expected of the long-sought triplet state of *N*-tosyl-3,4-dimethylenepyrrole **1b**. The nature of the other two triplets in the **b** series is discussed below. In extensions of this work, we also have prepared the corresponding persistent singlet and triplet states from the *N*-brosyl precursor **5c**,<sup>1a</sup> and we have developed a new synthesis (Scheme 1) of 2-aryl-*N*-tosyl-3,4-dimethylenepyrrolo-diazene, e.g., **5d**. The latter compound serves as a suitable precursor of the biradical *N*-*p*-toluenesulfonyl-2-phenyl-3,4-dimethylenepyrrole **1d** and now also can be used to generate both singlet and triplet species.

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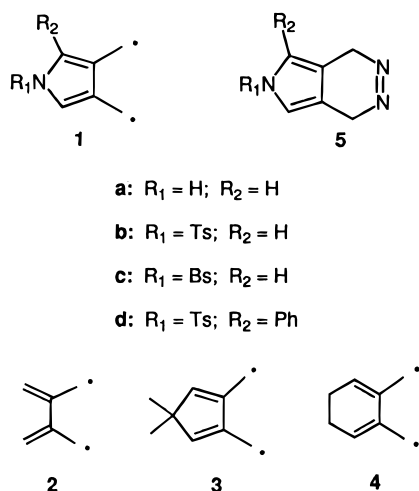
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<sup>†</sup> Current address: Department of Chemistry, Salisbury State University, Salisbury, MD 21801.

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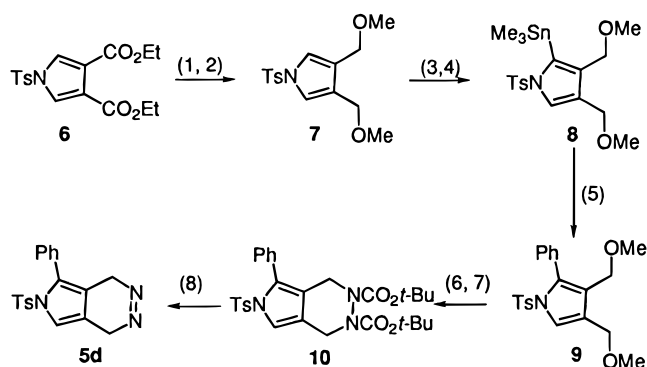


**Synthesis of Diazene 5d (Scheme 1).** The first four steps of Scheme 1 leading to the trimethylstannyl derivative **8** are identical to those<sup>1d</sup> in the synthesis of 1,3-di-2-pyrrolybenzenes. The path (**9** → **5d**) to the phenyl derivatives in Scheme 1 used a cross-coupling with iodobenzene (instead of 1,3-diiodobenzene, which was used<sup>1d</sup> to enter the 1,3-di-2-pyrrolybenzene series). Conversion to the bis-carbamate **10** and the diazene **5d** followed well precedented<sup>1</sup> steps.

**ESR Spectroscopic Characterization of Triplet Species Generated by Photolysis of Diazene Precursors 5b–d.**<sup>1a</sup> For ease of reference, the three types of triplet ESR spectra encountered in this work are designated by the relative magnitudes of their zero-field splitting (zfs) parameters  $|D/hc|$  as small (S), medium (M), or large (L), respectively. The substitution pattern of the biradical and its precursor is designated as **b**, **c**, or **d**, as in **1b–d** and **5b–d**. Scheme 2 shows the assignments of structure to the carriers of the three types of spectra in the **b** series. The assignment of the widest spectrum, **Lb**, to the *N*-tosyl-3,4-dimethylenepyrrole biradical **<sup>3</sup>1b** rests upon the agreement between the observed and calculated ESR zero-field splitting (zfs) parameter  $|D/hc|$  and also upon chemical trapping experiments, which point to an intact *N*-tosyl-3,4-dimethylenepyrrole structure. The other two triplet species, the carriers of the narrower spectra **Sb** and **Mb**, although less firmly identified, are consistent with diazenyl biradical structures **<sup>3</sup>11b** and **<sup>3</sup>12b**.

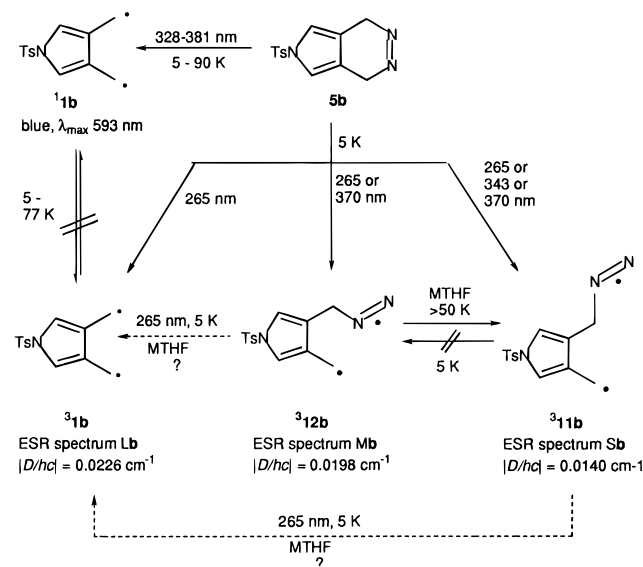
**Generation of Diazenyl Biradical Triplet Species <sup>3</sup>11b and <sup>3</sup>12b and of *N*-Tosyl-3,4-dimethylenepyrrole Biradical <sup>3</sup>1b in the Photolysis of Diazene 5b (Scheme 2).** The azo chromophore of *N*-tosyl diazene **5b** shows a broad UV–vis band with maxima at 370, 343, and ~300 nm. As has been described,<sup>1</sup> 370 nm irradiation in glassy matrices at 77 K generated singlet **1b**, an ESR-silent, blue transient,  $\lambda_{\max}$  593 nm. Table 1 summarizes our studies of the effects of matrix, wavelength, and temperature on the course of the photo-deazetation. It is convenient to divide the data into three groups according to irradiating wavelength:

**1. Irradiations at 340–345, 366 (Band-Pass Filtered), or 370 nm.** These generated spectra **Sb** and/or **Mb**, depending on temperature. Thus, ESR examination of a matrix of **5b** in EA glass (diethyl ether–ethanol) that had been irradiated briefly at 340 nm at 77 or at 5 K showed a strong four-line signal assignable to the  $\Delta m_s = 1$  transitions of a randomly oriented triplet species. This spectrum, **Sb**, also could be seen by irradiation at 340–345 nm of diazene **5b** in MTHF glasses at 77 K (Figure 1 **Sb**). Neither the EA nor the MTHF preparations from the 340–345 nm photolyses showed the blue color or the UV–vis maximum at 593 nm characteristic of the singlet

Scheme 1<sup>a</sup>

<sup>a</sup> **Methods.** (1) DIBAL,  $\text{CH}_2\text{Cl}_2$ , 81%. (2) MeI,  $\text{Ag}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ , 85%. (3) NBS, THF,  $-72^\circ\text{C}$ , 83%. (4) BuLi, THF,  $-78^\circ\text{C}$ ,  $\text{Me}_3\text{SnCl}$ , 100%. (5)  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ , PhI, 2-methyl-2-pyrrolidinone, 27%. (6)  $\text{Ph}_3\text{PBr}_2$ , 57%. (7)  $(t\text{-BuO})_2\text{CN}(\text{K})\text{N}(\text{K})\text{CO}_2t\text{-Bu}$ , 59%. (8) HCl,  $\text{Et}_2\text{O}$ ,  $\text{MeO}_2\text{CN}=\text{NCO}_2\text{Me}$ , 29%.

## Scheme 2

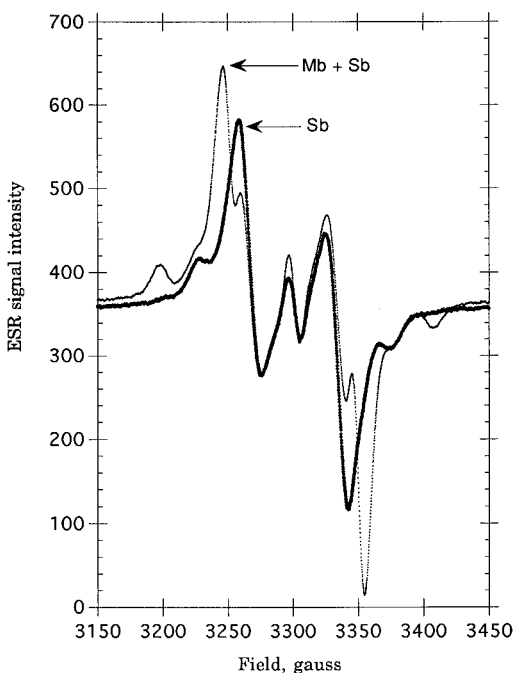


**Table 1.** Generation of Triplet Species by Irradiation of Diazene **5b**

matrix	$h\nu$ , nm <sup>a</sup>	$T$ , K	obsd ESR spectrum
EA <sup>b,c</sup>	343–345	5, 77	<b>Sb</b>
propanols <sup>d</sup>	265	5, 85, or 90	<b>Lb + Sb</b>
	230–325 <sup>j</sup>	5	<b>Lb + Mb + Sb</b> <sup>e</sup>
Freons <sup>e</sup>	265	5	<b>Lb (+ Sb?)</b>
	230–325 <sup>j</sup>	5	<b>Lb + Mb + Sb</b> <sup>e</sup>
MTHF <sup>f</sup>	265	5	<b>Lb + Mb + Sb</b>
	265	80	<b>Lb + Sb</b>
	230–325 <sup>j</sup>	5	<b>Lb + Mb + Sb</b> <sup>e</sup>
	366 <sup>k</sup>	5	<b>Mb + Sb</b> <sup>h</sup>
	370	5, 90 <sup>i</sup>	<b>Mb + Sb</b> <sup>h</sup>

<sup>a</sup> Methods of irradiation are described in the Experimental Section. <sup>b</sup> Diethyl ether–ethanol (1:1 v:v). <sup>c</sup> Reference 1. <sup>d</sup> PrOH:*i*-PrOH (2:3 v:v). <sup>e</sup>  $\text{CCl}_3\text{F}:\text{CF}_2\text{BrCF}_2\text{Br}$  (1:1 v:v). We thank M. S. Platz for suggesting this matrix. <sup>f</sup> 2-Methyltetrahydrofuran. <sup>g</sup> This preparation was visibly purple. <sup>h</sup> This preparation was visibly blue. <sup>i</sup> Observed by signal accumulation (see text). <sup>j</sup> 1 M  $\text{NiSO}_4$  solution filter, main transmission 230–325 nm. We thank P. Vaccaro for suggesting the use of a solution filter. <sup>k</sup> Glass band-pass filter with main transmission 328–381 nm.

biradical **<sup>1</sup>1b**. The ESR signals persisted for many hours at 77 K in the dark. Irradiation of **5b** in MTHF at 366 or 370 nm gave the **Sb** and **Mb** spectra also (see below), but the samples were visibly blue, because of the presence of the singlet biradical **<sup>1</sup>1b**.



**Figure 1.** Mb + Sb. ESR spectrum obtained by band-pass filtered (peak transmission 328–381 nm) or monochromatic ( $370 \pm 5$  nm) irradiation of diazene **5b** in MTHF glass at 5 K. The  $\Delta m_s = 2$  region is not shown. Sb. ESR spectrum obtained by raising the temperature of the preparation Mb + Sb to 75 K and re-cooling to 5 K. The  $\Delta m_s = 2$  region is not shown. The same Sb spectrum is obtained by 343 nm irradiation of **5b** at 5 K.

**2. Irradiations at 265 nm.** These generated predominantly spectrum Lb, but Sb and Mb could be observed under proper conditions. The samples were colorless or yellow, and the 593 nm band of **1b** was not seen in the UV–vis spectrum.

**3. Irradiations with Broad-Band Light, NiSO<sub>4</sub>-Filtered, Main Transmission at 230–325 nm, at 5 K.** These generated all three spectra Sb, Mb, and Lb. The preparations were colorless or yellow and showed no absorption in the 590 nm region of the UV–vis spectrum.

**Diazenyl Biradicals **11b** and **12b**, Carriers of the ESR Spectra Sb and Mb.** We consider first the spectrum Sb, which as described above, was formed cleanly in the 340–345 nm photolysis of diazene **5b** at 77 and 5 K. The Sb spectrum (Figure 1 Sb) is characterized by the zfs parameters  $|D/hc| = 0.0140 \text{ cm}^{-1}$  ( $2D' = 302 \text{ G}$ ),  $|E/hc| \sim 0$ . Although the nominally “forbidden”  $\Delta m_s = 2$  transition was difficult to see at 77 K, it was readily visible at 5 K. Even at 77 K, a weak  $\Delta m_s = 2$  resonance could be observed in matrices containing ethyl iodide, a heavy-atom solvent, presumably because of spin-orbit-mediated partial relaxation of the selection rule.

Although a triplet spectrum now was undoubtedly being generated, the result again was frustrating, because we were soon convinced that spectrum Sb was not associated with triplet *N*-tosyl-3,4-dimethylenepyrrole **3b**. That species should have shown (see below) a *D* value near  $0.025 \text{ cm}^{-1}$ , which would correspond to a splitting between the outermost lines ( $2D'$ ) almost twice that observed in spectrum Sb. Although not structurally diagnostic in direct terms, the zfs of Sb suggests that the average separation of the unpaired electrons in its carrier must be greater than that in **3b**. The diazenyl biradical<sup>7</sup> structure **311b**, resulting from cleavage of only one of the C–N bonds of the diazene **5b**, would be consistent with this feature of the Sb ESR spectrum and with the method of synthesis by photoactivation of the diazene chromophore of **5b**.

Spectrum Sb also could be discerned in 366–370 nm photolyses of **5b** at 5 K and, faintly, even at 90 K, by digital

accumulation of signals generated in continuous photolyses (see Table 1). We soon noticed a second triplet spectrum, Mb, superimposed upon spectrum Sb in some of the samples. This was especially clear in the spectra of samples prepared by irradiation at 5 K (Figure 1). As judged by the zfs parameter of Mb,  $|D/hc| = 0.0198 \text{ cm}^{-1}$  ( $2D' = 404 \text{ G}$ ), the two odd electrons in the carrier of Mb are closer together than those in the carrier of the narrow triplet signal Sb. We think it is likely that the carrier of Mb is **312b**, a conformational isomer of **11b** (Scheme 2).

The proximal and distal conformations assigned, respectively, to biradicals **11b** and **12b** are only schematic. They symbolize the inferences that the C–N–N angles, by analogy to theoretically predicted<sup>8–10</sup> angles near  $120^\circ$  for simple diazenyl radicals, are significantly bent, and that the larger *D* value for the proximal biradical **12b** (spectrum Mb) relative to the distal biradical **11b** (spectrum Sb) results from a closer average propinquity of the two unpaired electrons.<sup>11a</sup> Occupation of a  $\sigma$ -orbital by the N-centered electron<sup>8–10</sup> and of a  $\pi$ -orbital by the C-centered electron<sup>11b</sup> also seem likely additional features of these diazenyl biradicals.

**Thermal Interconversion of the Two Diazenyl Biradical Conformers.** We have observed a thermal transformation of the Mb spectrum into the Sb spectrum. Figure 1 shows that short irradiation at 366 nm of an MTHF glass of diazene **5b** at 5 K generates an ESR trace in which Sb and Mb are superimposed. Raising the temperature of this sample to 40–50 K decreases the intensity of the Mb signals, but this is not entirely a Curie Law effect: The intensity of the Sb signal increases at the same time, and if the temperature is allowed to rise briefly to 75 K, the only visible triplet spectrum is the “narrow” signal Sb. Prompt cooling of the sample back to 5 K does not restore the Mb spectrum, but the Sb spectrum now (Figure 1Sb) is more intense than it was originally. The Sb spectrum itself slowly fades above 70 K (see below).

We interpret these changes as a thermal conformational isomerization of **312b** to **311b** (Scheme 2). Since the Sb and Mb spectra overlap appreciably (Figure 1), one cannot be sure that the intensity gained by the Sb spectrum through the cycle of temperature 5 K  $\rightarrow$  75 K  $\rightarrow$  5 K corresponds exactly to the intensity lost from the Mb spectrum. It is therefore possible that a competitive thermal reaction of **312b**, the carrier of the Mb spectrum, could convert it in part to some other product that is ESR-silent. Nevertheless, conversion to **311b**, the carrier of the Sb spectrum, must account for the major part, if not all, of the thermal reaction that consumes **312b**.

The kinetics of the Mb  $\rightarrow$  Sb transformation are complex and cannot be fitted well to either a first- or a second-order rate law, probably because of a distribution of the immobilized triplet molecules over nonequivalent sites in the matrix.<sup>11c</sup> For this reason, a determination of true rate constants and an

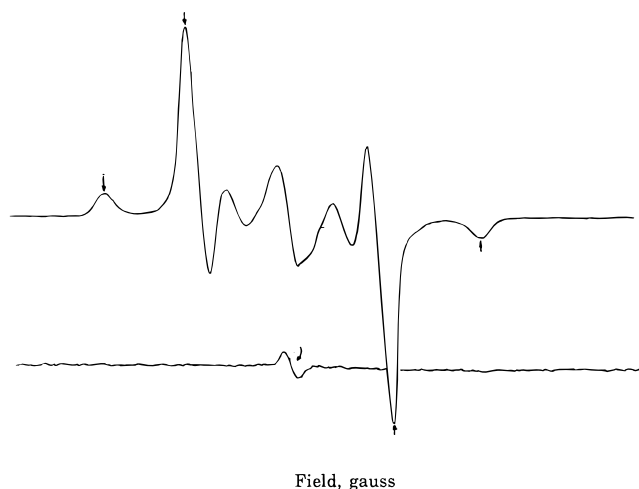
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**Figure 2.** ESR spectrum obtained by 265 nm irradiation of *N*-tosyl diazene **5b** in EIA glass at 77 K for 1.5 min. The spectrometer frequency is 9.296 GHz. The upper trace shows the  $\Delta m_s = 1$  region; the peaks of the **Lb** spectrum associated with  $^3\mathbf{1b}$  are marked with arrows and occur at 3075, 3184, 3430, and 3558 G. The unlabeled peak in the middle of the spectrum is associated with impurities formed in the photolysis. The two peaks flanking it are at the same positions as the main peaks of the **Sb** spectrum (see Figure 1). The lower trace is offset and shows the  $\Delta m_s = 2$  region centered at 1662 G.

Arrhenius activation energy have not been feasible. By forcing the data to first-order form ( $r = 0.96$ ), we derive a rate “constant” for the  $\mathbf{12b} \rightarrow \mathbf{11b}$  reaction at 57 K of  $2.77 \times 10^{-5} \text{ s}^{-1}$ , which corresponds to a free energy of activation of 4.4 kcal/mol. Anticipating criticism of this crude kinetic method, we note that although site nonuniformity can lead to rate “constants” that differ by a factor of 100 or more,<sup>11c</sup> the effect on  $\Delta G^\ddagger$  at these temperatures is quite small. For example, rate constants of  $10^{-4}$  and  $10^{-6} \text{ s}^{-1}$  at 57 K correspond to  $\Delta G^\ddagger = 4.2$  and 4.7 kcal/mol, respectively.

Similarly, the essentially unidirectional nature of the rearrangement of  $^3\mathbf{12b}$  to  $^3\mathbf{11b}$  should not cause surprise, since at low temperatures, small energy differences, such as could be associated with conformational isomerism, readily could account for this result. For example, we estimate the ESR detection limit for  $^3\mathbf{12b}$  remaining after the rearrangement has reached  $^3\mathbf{12b} \text{--} ^3\mathbf{11b}$  equilibrium at 75 K to be about 5%, corresponding to an equilibrium constant of about 20 in favor of **11b**.  $\Delta G^\circ$  for the conformational isomerization therefore could be as small as 0.45 kcal/mol.

**A Kinetically Stable Triplet State of *N*-Tosyl-3,4-dimethylenepyrrole **1b**.** Brief irradiation of the *N*-tosyl diazene **5b** in MTHF or other solvent glasses at wavelengths in the range 250–295 nm does not produce a detectable blue color or a UV–vis maximum at 593 nm characteristic of the singlet **1b**. Instead, these preparations show a four-line ESR spectrum, **Lb**, characteristic of a *third* triplet species. The zfs parameter,  $|D/hc| = 0.0226 \text{ cm}^{-1}$  ( $2D' = 483 \text{ G}$ ), is the largest of the three triplet spectra. The spectrum can be fitted to a Hamiltonian with small or zero values of the parameter  $|E/hc|$  ( $< 0.0005 \text{ cm}^{-1}$ ). At 265 nm in EIA glass, for example, 90 s of irradiation at 77 K produces the spectrum shown in Figure 2, observed at a microwave frequency of 9.296 GHz. A weak half-field transition ( $\Delta m_s = 2$ ) associated with the **Lb** spectrum is seen centered around 1662 G. This confirms the assignment of a triplet state to the carrier of the **Lb** spectrum.<sup>11a</sup>

The peak near 3317 G we assign to a doublet or radical pair impurity, which probably arises from photodissociation of the S–N bond of the *N*-tosyl group. This type of reaction is

responsible for the well-known<sup>12</sup> photo deprotection of *N*-arenesulfonamides (see below).

Under some conditions, the  $\Delta m_s = 1$  region of the **Lb** spectrum shows six lines, of which two (3233 and 3392 G) flank the impurity peak in the interior of the spectrum and are not associated with the new triplet carrier of **Lb**, since their intensities relative to those of the lines of **Lb** are variable. The positions of the 3233 and 3392 G lines of **Lb** correspond exactly to those of the strong inside lines (3227 and 3396 at 9.294 GHz) of the previously described **Sb** triplet spectrum associated with the distal diazenyl biradical **11b** (see Figure 1). The weak outer lines of the narrow **Sb** triplet spectrum, expected near 3164 and 3466 G (Figure 1), are not readily seen in the spectrum (Figure 2) of the 265 nm product because they are overlapped by absorptions of **Lb**. Apparently, the 265 nm irradiation in MTHF leads to two different triplets, the carriers of **Lb** and **Sb**.

In the photochemistry of diazene **5b** that leads to the triplet spectrum **Lb**, the diazene unit seems to be a necessary structural feature of the precursor. For example, irradiation at 265 nm and 77 K of the model compound *N*-tosylpyrrole generates strong signals in the  $g = 2$  region which we assign to doublet or radical pair species produced in the photodesulfonylation of sulfonamides,<sup>12a–d</sup> but no trace is seen of a triplet signal of sufficiently large zfs to account for the signal **Lb** observed in the irradiation of **5b**. This finding argues against several possible assignments of the **Lb** triplet signal to species derived from hypothetical processes localized to the pyrrole and arenesulfonyl moieties.

The assignment of the structure *N*-tosyl-3,4-dimethylenepyrrole  $^3\mathbf{1b}$  to the carrier of the triplet spectrum **Lb** is consistent with its zero-field splitting. The  $D$  value matches closely the value  $|D/hc| = 0.0256 \text{ cm}^{-1}$  calculated theoretically for *N*-benzenesulfonyl-3,4-dimethylenepyrrole by a point–dipole approximation procedure (Table 2). Moreover, it is close to those experimentally measured and theoretically calculated for other known TME derivatives. Although this type of calculation is not calibrated for  $\sigma$ -biradicals and hence is not reliable for prediction of the zfs of the diazenyl biradicals  $^3\mathbf{11b}$  and  $^3\mathbf{12b}$ , the  $D$  values for these species, which are 1,5- or 1,6-biradicals, would be expected to be smaller than that for  $^3\mathbf{1b}$ , a 1,4-biradical, in agreement with observation.







Since the triplet  $^3\mathbf{1b}$  does not have structural 3-fold symmetry, the near-zero value of  $|E/hc|$  observed suggests a near-equality of two of the nominally anisotropic spin–dipolar interactions. This presumably is the result of an accidental near-degeneracy of two of the Cartesian directions in the molecular framework.<sup>11a</sup> Similarly, the ESR spectrum of the triplet brosyl derivative **1c** (see below) shows only four lines, corresponding to  $|E/hc| \sim 0$ . This degeneracy is broken, however, in the case of the *N*-tosyl-2-phenyl-3,4-dimethylenepyrrole biradical  $^3\mathbf{1d}$  (see below), whose ESR spectrum shows six lines, corresponding to  $|E/hc| > 0$ .

Like the blue singlet form of biradical  $^1\mathbf{1b}$ ,<sup>1</sup> the triplet  $^3\mathbf{1b}$  was stable in the dark for weeks at 77 K but was photolabile. Irradiation at 400 nm of a sample of  $^3\mathbf{1b}$  caused disappearance of the **Lb** ESR signal. The impurity peaks in the center of the spectrum remained after photobleaching of the **Lb** spectrum, thereby demonstrating that they arise from a different carrier.

New ESR signals were not detected from the photobleaching reaction, and it is tempting to conclude that the photoproducts of the **Lb** carrier  $^3\mathbf{1b}$  are ESR-silent. However, since the **Lb**

(12) (a) Abad, A.; Mellier, D.; Pète, J. P.; Portella, C. *Tetrahedron Lett.* **1971**, 4555. (b) Mellier, D.; Pète, J. P.; Portella, C. *Tetrahedron Lett.* **1971**, 4559. (c) Umezawa, B.; Hoshino, C.; Sawaki, S. *Chem. Pharm. Bull.* **1969**, *17*, 1115, 1120; **1970**, *18*, 182. (d) Art, J. F.; Kestemont, J. P.; Soumillion, J. Ph. *Tetrahedron Lett.* **1991**, 32, 1425.

**Table 2.** Values of the Zero-Field Splitting Parameter  $|D/hc|$  ( $\text{cm}^{-1}$ ) for TME Derivatives

compd	$ D/hc $ , obsd	$ D/hc $ , calcd <sup>h</sup>
	0.025 <sup>a</sup>	0.0236; <sup>d,f</sup> 0.025 <sup>e</sup>
<b>2</b>		
	0.0259 <sup>b</sup>	<i>g</i>
<b>3</b>		
	0.0204, <sup>b</sup> 0.024 <sup>c</sup>	0.025 <sup>e</sup>
<b>4</b>		
	0.0226 <sup>d</sup>	0.0256 <sup>d,f,h,i</sup>
<b>1b</b>		
	0.0231 <sup>d</sup>	<i>g</i>
<b>1c</b>		
	0.0187 <sup>d</sup>	<i>g</i>
<b>1d</b>		

<sup>a</sup> Reference 3a. <sup>b</sup> Reference 3c. <sup>c</sup> Reference 3b. <sup>d</sup> This work. <sup>e</sup> Rule, M.; Matlin, A. R.; Seeger, D. A.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron*, **1982**, 38, 787. A value of  $0.0255 \text{ cm}^{-1}$  has recently been calculated for this molecule by methods requiring no empirical scaling factor: Prasad, B. L. V.; Radhakrishnan, T. P. *J. Mol. Struct. (Theochem)* **1996**, 361, 175. <sup>f</sup> The empirical divisor (see ref 5e) used in this work was 2.11. <sup>g</sup> Not calculated. <sup>h</sup> Details of the calculations are given in the Supplementary Material to ref 1a and in ref 6b. <sup>i</sup> Calculated for the *N*-benzenesulfonyl-3,4-dimethylenepyrrole biradical.

spectrum represents only about 1.6% conversion of diazene **5b** to biradical <sup>3</sup>**1b** (see below), it is possible that new triplet species might be present in the photolysate of <sup>3</sup>**1b** but at too low a concentration to be detected. The photobleaching of <sup>3</sup>**1b** does not produce any visible blue color, such as would be associated with the singlet state of **1b**.

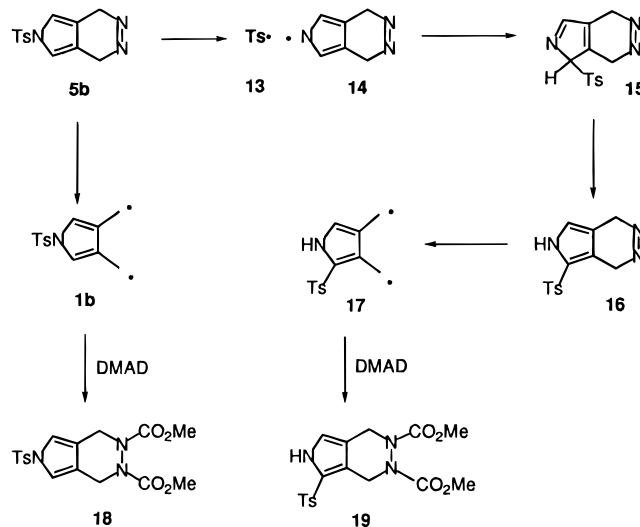
**Structural Assignments to the Carriers of the ESR Spectra Lb, Mb, and Sb. A. Spectroscopic Evidence.** For review, we list the principal spectroscopic bases for the assignments given as, respectively, <sup>3</sup>**1b**, <sup>3</sup>**12b**, and <sup>3</sup>**11b**:

(1) The diazene unit of the precursor **5b** is a necessary structural feature for the production of any of the three triplet spectra. No such spectra are observed upon irradiation of model compounds such as *N*-tosylpyrrole or the cycloadducts of *N*-tosyl-3,4-dimethylenepyrrole with alkenes. This suggests that the chemical change leading to any of the triplets is initiated by a photoreaction of the diazene unit.

(2) The carriers of the **Sb** and **Mb** spectra are formed by irradiation in the diazene chromophore with light of wavelength 340–370 nm. This again is consistent with a process involving cleavage of a C-to-N=N bond. In the photodeazetation of acyclic and cyclic 1,2-diazenes, a variety of mechanistic studies<sup>7</sup> have provided persuasive indirect evidence implicating diazenyl radicals and biradicals, respectively. A significant confirmatory observation comes from time-resolved coherent anti-Stokes Raman spectroscopy (CARS)<sup>8</sup> of the evolved N<sub>2</sub> in such processes.

(3) The *D* values of the **Sb** and **Mb** spectra are smaller than that of the **Lb** spectrum, in accord with a greater separation of the unpaired electrons in the biradicals responsible for the former two spectra.

(4) The occurrence and rate of the transformation of the **Mb** carrier to the **Sb** carrier are consistent with a conformationally isomeric relationship of the two.

**Scheme 3**

(5) The *D* value of the **Lb** spectrum is in good accord with that predicted by a point-dipole approximation that has given agreement with a number of known  $\pi$ -conjugated triplet molecules (Table 2).

In the next section, we provide support for the assignment of the **Lb** spectrum to <sup>3</sup>**1b**. For the present, no such additional evidence is available for the diazenyl biradicals **11b** and **12b**, the putative carriers of **Sb** and **Mb**. It will be obvious, for example, that the observation of nitrogen hyperfine splitting in the latter spectra would strengthen the assignments. However, hyperfine splitting often is not seen under the broad lines of such powder spectra, so that its absence is more a source of regret than of surprise. As is described in the Supporting Information, other confirmatory findings would be a demonstration that either or both of the diazenyl biradicals could be thermally or photochemically converted to the *N*-tosyl-3,4-dimethylenepyrrole biradical **1b**. We note here that attempts to demonstrate photoconversion of diazenyl biradicals <sup>3</sup>**11b** or <sup>3</sup>**12b** to <sup>3</sup>**1b** by irradiation at 265 nm, the wavelength needed to generate <sup>3</sup>**1b**, are frustrated by the fact that, as we already know, the spectrum **Lb** associated with <sup>3</sup>**1b** appears upon 265 nm irradiation of diazene **5b**, without prior generation of spectra **Sb** or **Mb**. Therefore, the appearance of **Lb** upon 265 nm irradiation of a preparation of **Sb/Mb**, which normally contains unreacted **5b**, would not be decisive. Further discussion of the carriers of the **Sb** and **Mb** spectra, putatively **11b** and **12b**, including the nature of the reaction that occurs above 70 K and eventually causes the **Sb** ESR signal to vanish, is given in the Supporting Information.

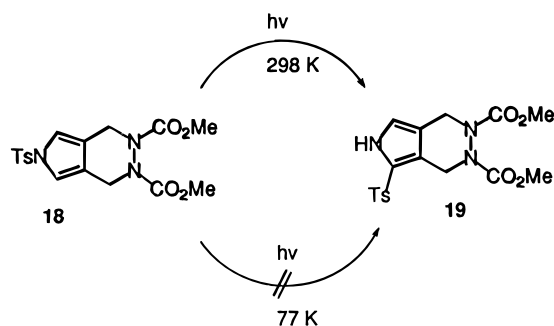
**B. Chemical Evidence for the Structure of the Lb Carrier.** At the present stage of the study, the most significant of the three triplets is the carrier of the **Lb** spectrum, which we have assigned the *N*-tosyl-3,4-dimethylenepyrrole structure <sup>3</sup>**1b**. We now describe experimental observations which exclude the most plausible alternative and which demonstrate that it is possible to involve the carrier of the **Lb** triplet in a cycloaddition reaction that gives a product containing the intact *N*-tosyl-3,4-dimethylenepyrrole structure.

**Exclusion of a Rearranged Structure.** Probably the most vexatious of the alternatives to <sup>3</sup>**1b** would be a rearranged structure, such as could be imagined to arise by the pathway shown in Scheme 3. Hypothetically (but not necessarily), this might occur through the pair of radicals **13–14**. Recombination in **13–14** could lead to an isopyrrole **15**, which after tautomerization to the rearranged pyrrole **16**, could undergo deazetation

to the biradical **17**. The overall structural result would be to interchange the tosyl group at N with the hydrogen at C<sub>2</sub> by way of a nitrogen analog of a photo-Fries rearrangement. Several examples of reactions analogous to **5b** → **16b**, especially in *N*-tosylcarbazoles, have been observed.<sup>13a,b</sup>

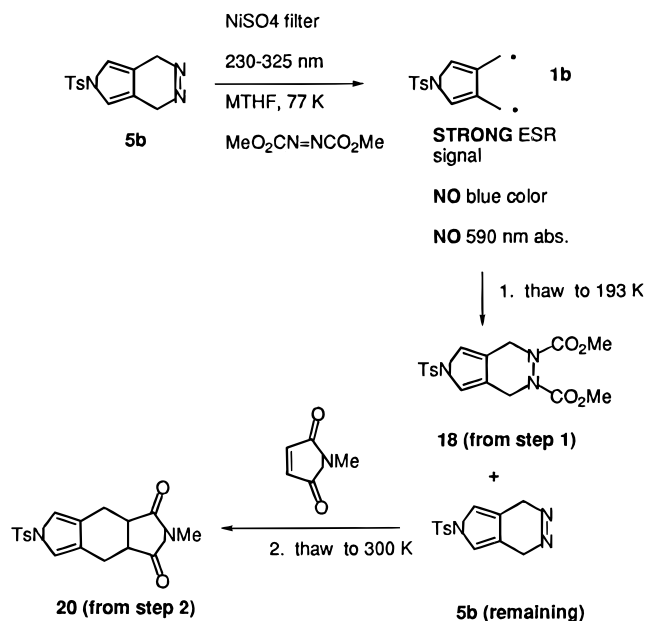
However, several aspects of the formulation of the carrier of our ESR spectrum **Lb** as the rearranged structure **17** are improbable. The reactions leading to the observed triplet species are observed to occur at 5 K, so that either there would have to be several independent photochemical steps in sequence, or any thermal steps, for example, the 1,5-sigmatropic hydrogen shift **15** → **16**, must have activation energies of <0.3 kcal/mol or must occur by thermal tunneling processes. Also, there is no obvious reason why biradical **17** should have an accessible triplet state, since the electron-withdrawing Ts substituent is no longer on the pyrrole nitrogen.<sup>1</sup> Perhaps the most implausible requirement is that the rearranged diazene **16** must undergo deazetation to biradical **17** but the original diazene **5b** must not undergo deazetation to biradical **1b**. Despite these arguments, the possibility of such a rearrangement was of sufficient concern to motivate additional scrutiny.

**By Analogy.** In the first experiment of this series, we studied the photolysis of the bis-carbamate **18** as a model for the diazene **5b**, with the rationale that the carbamate units should have no independent photochemistry under the conditions we would use. This would provide a clear field for the observation of the suspected photo-Fries rearrangement without the deazetation that inevitably accompanies photolysis of the diazene. We found that in any of several different solvents (benzene, CH<sub>3</sub>CN, THF, MTHF, or MeOH), irradiation of the bis-carbamate **18** at room temperature with light from a 1000 W Hg–Xe arc (unfiltered or NiSO<sub>4</sub>-filtered) did indeed give the rearranged bis-carbamate **19** in about 20% yield after chromatographic isolation. Some starting **18** was recovered and, in some of the solvents, a trace of the detosylated bis-carbamate was formed. Significantly, however, when irradiation of bis-carbamate **18** was carried out either with 366 nm light (other conditions unchanged) or with NiSO<sub>4</sub>-filtered light in MTHF matrix at 77 K, none of the rearranged bis-carbamate was formed, and only the starting material **18** was recovered. Thus, the photorearrangement of the bis-carbamate **18** is effectively shut down in low-temperature matrices. By analogy, the hypothetical rearrangement of the diazene **5b** (Scheme 3) under these conditions is unlikely.<sup>14a</sup>



**Directly. The Carrier of the Lb ESR Spectrum Contains the Intact 3,4-Dimethylenepyrrole Unit.** In addition to this analogical argument, we have been able to provide direct evidence that photolysis of the diazene **5b** (Scheme 3) does not produce appreciable quantities of rearranged diazene **16** or its cognate biradical **17**. Capture of **17** by an appropriate trapping agent, dimethyl azodicarboxylate (DMAD), would have led to

#### Scheme 4



the now known bis-carbamate **19**. However, we found that photolysis (at various wavelengths) of diazene **5b** at 77 K in MTHF matrix in the presence of 2.5 equiv of dimethyl azodicarboxylate (DMAD) followed by warming to room temperature gave as a trapping product only the unrearranged bis-carbamate **18** and none of the rearranged one **19** (Scheme 4).

To demonstrate the connection between the carrier of the **Lb** ESR spectrum and the *N*-tosyl-3,4-dimethylenepyrrole structure, we carried out a series of experiments (Scheme 4) in which the triplet carrier <sup>3</sup>**1b** of the ESR spectrum was generated as a reactive intermediate in the absence of the blue singlet <sup>1</sup>**1b**. As we have previously shown, irradiation with monochromator-filtered light of wavelength 265 nm of an MTHF matrix of diazene **5b** at 77 K (see Table 1) gave the **Lb** ESR spectrum of <sup>3</sup>**1b**, but no blue color or 590 nm UV–vis absorption of the singlet <sup>1</sup>**1b** could be detected. Because the 265 nm emission of the Hg–Xe photolamp is strongly reversed, and because the transmission of the monochromator is only about 10% at this wavelength,<sup>18</sup> the irradiance is very low and the amount of triplet actually generated under these conditions is only 1.6% by ESR spin count. We have not been able to detect any trapping product that can be ascribed to a photogenerated biradical under

(14) (a) To circumvent the assumptions associated with the use of a model reaction, it would be desirable to know something of the chemistry of the hypothetical rearranged diazene **16** itself. On a small scale, we have tried to prepare this substance from the rearranged bis-carbamate **19**, but our usual procedures of hydrolysis and oxidation so far seem to give only the corresponding hydrazone (NMR identification). We suspect that the presence of the conjugated tosyl group at C<sub>2</sub> renders the hydrogens adjacent to the diazene linkage of **16** so acidic that rapid tautomerization to the more stable hydrazone ensues. (b) A reviewer has asked whether the radical-pair **13**–**14** (Scheme 3) might be the carrier of the **Lb** ESR spectrum. Substantial evidence against this possibility is available. First, the *D* value of the **Lb** spectrum, 0.0226 cm<sup>-1</sup>, is large for a radical pair and would require that the radical partners remain close together. Since the same *D* value is observed in several different matrices, one would have to postulate that, fortuitously, the separation remains the same in all these media. Second, as already has been stated, no such triplet spectra are seen in the photolyses of model compounds such as *N*-tosylpyrrole or the cycloadducts of biradical **1b** and alkenes. Third, to form, in the dark, the observed trapping product **18** from the **Lb** triplet preparations allegedly containing the **13**–**14** radical pair would require some such mechanism as thermal deazetation of the radical **14** at 193 K, followed by cycloaddition of the resulting triradical, followed by recombination of the resulting adduct monoradical with radical **13**. We consider these joint requirements sufficient to render the radical-pair assignment highly improbable.

(13) (a) Horspool, W. M. In *The Chemistry of Sulphonic Acids, Esters and their Derivatives*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1991; Chapter 13. (b) Pillai, V. N. R. *Org. Photochem.* **1987**, *9*, 225.

these monochromatically filtered conditions. However, with NiSO<sub>4</sub>-filtered irradiation (230–325 nm), the light intensity was much greater, and the ESR signal intensities of the resulting **Lb** and **Sb** spectra were at least 5 times greater than those seen in a comparable time of irradiation with monochromator-filtered 265 nm light. There is no doubt that much higher concentrations of triplet species were being produced in the NiSO<sub>4</sub>-filtered irradiation, but the characteristic visible blue color and 590 nm UV–vis band of the singlet <sup>1</sup>**1b** still did not appear.

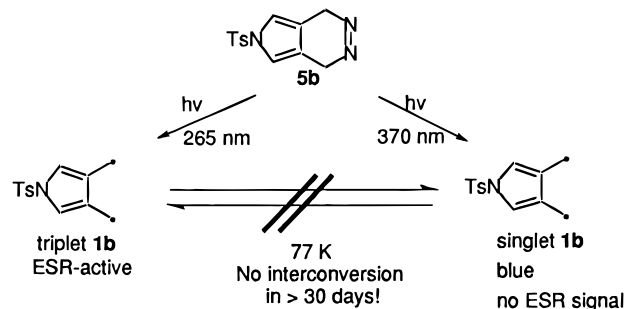
The next task was to show that the bis-carbamate trapping product **18** observed in the experiments of Scheme 4 arose from photochemically generated intermediates and not just from remaining unphotolyzed **5b** in the warm-up step. Accordingly, in the experiments of Scheme 4, the samples were warmed only to 193 K, a temperature below the threshold for thermal decomposition of the diazene **5b**. The remaining unphotolyzed **5b** was then scavenged by adding a swamping concentration (50 times the initial DMAD concentration) of a second trapping agent, *N*-methylmaleimide (NMM), and allowing the temperature to rise to 300 K. NMM is a faster diylophile than DMAD and therefore should be essentially (>99%) the exclusive trapping agent for any diyl liberated thermally at this point. If the photolyses actually were generating diyls in interceptable amounts, the ratio of photoproduct to thermal product (DMAD adduct **18** to NMM adduct **20**) should increase with increasing photolysis time. Experimentally, this was what we observed. The ratios were 22:78, 30:70, and 54:46, respectively, after 15, 30, and 60 m of photolysis. Again, the only DMAD product observed was the unrearranged bis-carbamate **18**. The HPLC analytical conditions were such that a peak at the known emergence time of the rearranged bis-carbamate **19** could have been detected at the level of <0.1% of the intensity of the band due to **18**.

If the ESR spectrum **Lb**, which we have assigned to <sup>3</sup>**1b**, were instead due largely (say a 10:1 ratio **17**:**1b**) to the rearranged biradical **17** (Scheme 3), then in order for unrearranged adduct **18** to be formed in the ratio of >1000:1 over rearranged adduct **19**, the reactivity of **1b** toward DMAD would have to be >10 000 times that of **17**. This seems unlikely. The more reasonable conclusion is that, in competition with deazetation, not even a trace of photorearrangement of **5b** to diazene **16** occurs at 77 K, under the photolysis conditions that produce the **Lb** ESR spectrum. When taken with the already listed, inherently implausible subsidiary hypotheses needed to sustain the proposal that the **Lb** ESR spectrum is associated with rearranged biradical **17**, the trapping results provide a persuasive basis for the straightforward structural assignment of biradical <sup>3</sup>**1b** as the carrier.<sup>14b</sup>

These experiments strongly suggest that DMAD can trap chemically either the triplet species responsible for the **Lb** ESR spectrum, or a species readily derived from that triplet, to give a product bis-carbamate **18** which contains an intact *N*-tosyl-3,4-dimethylenepyrrole structure. With reference to other attempts to trap <sup>3</sup>**1b**, which have uniformly led to products from <sup>1</sup>**1b** instead,<sup>1c</sup> it seems likely that the actual reactant in the present DMAD trapping experiments is the singlet <sup>1</sup>**1b** formed by intersystem crossing from <sup>3</sup>**1b** when the matrix is thawed to effect the cycloaddition, as already described.<sup>1a–c</sup> In sum, the observations link the carrier of the **Lb** ESR spectrum with the *N*-tosyl-3,4-dimethylenepyrrole structural unit.

**Long-Lived Spin Isomerism of the Singlet and Triplet States of *N*-Tosyl-3,4-dimethylenepyrrole **1b**.** The **Lb** ESR signal of <sup>3</sup>**1b** persists in the dark at 77 K for at least 1 month. Even in EIA-heavy-atom<sup>15</sup> solvent mixtures containing 1-bromopropane, iodoethane, or xenon at 77 K, the triplet preparations

### Scheme 5. Irradiations in Glassy Matrices



do not develop the blue color or UV–vis band ( $\lambda_{\max}$  590 nm) characteristic of the singlet form <sup>1</sup>**1b** after storage for days. Similarly, the blue preparations<sup>1</sup> of the singlet can be stored for extended periods at 77 K without developing any of the ESR spectrum of the triplet form (Scheme 5). If our structural assignments are correct, these experiments have generated independently the singlet and triplet forms of the same biradical, and interconversion of the spin isomers is slow on the time-scale of days or weeks. We now have devoted some effort to understanding the origins and implications of this long-lived spin isomerism.

One immediately obvious consequence of the slow interconversion is that serious doubt now is cast on attempts to assign the spin of the molecular ground state of biradical **1b**. For example, the widely used technique<sup>16,17</sup> of the Curie law plot attributes a triplet ground state (or an exact degeneracy of triplet and singlet) to a species whose ESR signal intensity is linear with reciprocal temperature. Equilibration was assumed by implication in the original application of ESR Curie plots,<sup>16</sup> and later, it was restated explicitly as a requirement.<sup>17d</sup> The present observations call attention to the fact that an ESR-active triplet not in rapid interconversion with another spin isomer can always be expected to give a linear Curie plot, whether or not it is the ground state. The time scale for "rapid interconversion" here is the investigator's pace of changing the temperatures and making the intensity measurements. Under conditions of slow interconversion, the ESR signal of such a triplet, like that of any kinetically stable paramagnetic species, then simply will respond linearly to reciprocal temperature.

The Supporting Information describes details of Curie law experiments on the *N*-tosyl-3,4-dimethylenepyrrole triplet **1b**. The slight downward curvature of the plot can be fitted formally to an energy separation  $E_T - E_S \approx 19$  cal/mol, on the usual (but now dubious) assumption of spin equilibrium between the triplet and some singlet. If this singlet is the blue species of  $\lambda_{\max} = 593$  nm, in a blue sample prepared by irradiation at 370 nm under specified conditions (see Supporting Information), an energy gap of 19 cal/mol would imply the presence of an amount

(15) For discussions of heavy-atom effects on intersystem crossing, see: (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969; Chapter 5. (b) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990; pp 24, 42. (c) Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 583. (d) Koziar, J. C.; Cowan, D. O. *Acc. Chem. Res.* **1978**, *11*, 334. (e) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: New York, 1978; Chapter 6.

(16) Bijl, D.; Kainer, H.; Rose-Innes, A. C. *J. Chem. Phys.* **1959**, *30*, 765.

(17) Reviews: (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969. (b) Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27. (c) Reference 11a. (d) Berson, J. A. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. II, p 482 ff.

(18) Oriol Equipment Catalog, Vol. II, Oriol Corporation, Stratford, CT, 1994; p 1–43.

of the triplet easily sufficient to detect by the characteristic ESR spectrum. Yet, such samples show no trace of an ESR triplet signal. We conclude, therefore, that either the small curvature in the Curie plot is artifactual (for example, a saturation effect) and the triplet has not achieved equilibrium with any other species, or if it has and the curvature is real, the species in equilibrium with the triplet is not the blue singlet already described.

**Incorporation of an Internal Heavy Atom. A Kinetically Stable Triplet Form of *N-p*-Bromobenzenesulfonyl-3,4-dimethylenepyrrole <sup>3</sup>**1c**.** Since the rate of intersystem crossing was not perceptibly increased by external heavy atoms in the matrix (see above), we attempted to achieve this end by incorporation of a heavy atom in the biradical itself. The *N-p*-bromobenzenesulfonyl (brosyl)-3,4-dimethylenepyrrole biradical **1c** was prepared from diazene **5c** by methods similar to those used for the preparation of the tosyl derivative **1b** from its precursor **5b**.

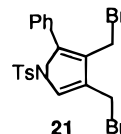
**Irradiation of **5c** at 340 and 370 nm.** The photochemistry of brosyl diazene **5c** at 77 K was essentially identical to that of the tosyl derivative **5b**. Irradiation of **5c** in MTHF at 77 K with 370 nm light gave a pale blue preparation which showed only a weak narrow ESR triplet spectrum, **Sc**. A much stronger **Sc** spectrum, with resonances at the same positions as before, was generated by irradiation at 340 nm. The  $\Delta m_s = 2$  transition was weak but visible at 77 K. The zfs parameters of the **Sc** spectrum,  $|D/hc| = 0.0140 \text{ cm}^{-1}$ ,  $|E/hc| \leq 0.0007 \text{ cm}^{-1}$ , matched those of the spectrum **Sb** of diazenyl biradical **11b** obtained by 340 nm irradiation of the *N*-tosyl diazene **5b**. Accordingly, we tentatively assign the diazenyl biradical structure **11c** to the carrier of the **Sc** ESR spectrum obtained by 340 nm irradiation of **5c**. This spectrum was still strong after having been stored in the dark for 14 days at 77 K.

**Irradiation of **5c** at 265 nm.** Irradiation at 265 nm of the *N*-brosyl diazene **5c** in MTHF matrix at 77 K gave rise to a strong four-line ESR signal of a new triplet species **Lc** superimposed on a weak central signal about 100 G wide associated with an impurity. The new four-line triplet signal was characterized by zfs parameters almost identical to those of **Lb**, the spectrum of the *N*-tosyl triplet <sup>3</sup>**1b**:  $|D/hc| = 0.0231 \text{ cm}^{-1}$ ,  $|E/hc| \leq 0.0005 \text{ cm}^{-1}$ . A weak half-field transition ( $\Delta m_s = 2$ ) also was observed. We assign the **Lc** spectrum to the *N*-brosyl-3,4-dimethylenepyrrole biradical <sup>3</sup>**1c**. The spectrum was observed at temperatures as low as 14 K and persisted with undiminished intensity for 15 days at 77 K. As has been reported in the accompanying article,<sup>1c</sup> the blue singlet form <sup>1</sup>**1c** does not give rise to any ESR resonances, even after long-term storage at 77 K.

It is possible that the heavy atom effect of bromine in the brosyl biradical **1c** does in fact accelerate intersystem crossing, but that even the increased rate remains too slow to detect. We must point out that the location of the bromine in <sup>3</sup>**1c** probably is not optimally conducive to the internal heavy atom effect, which would have been expected<sup>15c</sup> to be stronger with the bromine directly at a site of high spin density, namely C<sub>2</sub> of the pyrrole ring or the exocyclic methylene position. For the present, we can only state that our attempts to induce a discernible enhancement in the rate of intersystem crossing in this series by external or internal heavy atoms have been ineffectual.

**A Triplet State of *N*-Tosyl-2-phenyl-3,4-dimethylenepyrrole. Irradiation of **5d** at 345 and 370 nm.** We also have studied briefly the species obtained by photolysis of the *N*-tosyl-2-phenyl diazene **5d**. Irradiation at 370 nm in MTHF gave a visibly green preparation whose color persisted at 77 K but

rapidly disappeared when the matrix was thawed. UV-vis examination of the green matrix showed only weak broad absorption in the region 600–700 nm. By analogy to the cases of the 370 nm photolyses of the *N*-tosyl- and *N*-brosyl diazenes **5b,c**, it seems likely that the singlet biradical <sup>1</sup>**1d** is present. The weak optical absorption perhaps may indicate that only a low photostationary concentration of this species accumulates under these conditions, plausibly because of a secondary photoreaction analogous to that which photobleaches the singlet <sup>1</sup>**1b**. Further work would be needed to test this possibility. A somewhat stronger and better defined UV-vis spectrum was obtained when a glass of the dibromide **21** in MTHF containing



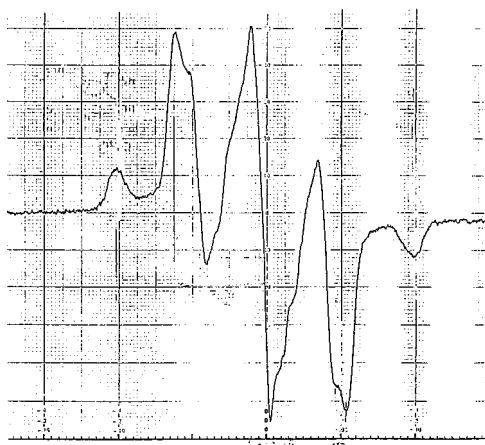
tetrakis(dimethylamino)ethylene at 77 K was irradiated<sup>19</sup> with Pyrex-filtered light:  $\lambda_{\text{max}}$  (nm) 400 (broad, strong), 640 (medium), and 795 (weak). It is possible that not all of these absorptions are caused by one species. We have not yet studied the chemistry of the singlet, but the UV-vis spectrum persists upon storage at 77 K.

ESR examination of the above sample obtained by irradiation at 77 K of the *N*-tosyl-2-phenyl diazene **5d** at 370 nm or of a sample irradiated at 345 nm showed the presence of a 4-line triplet spectrum **Sd** or **Md** with zfs parameters  $|D/hc| = 0.0129 \text{ cm}^{-1}$  and  $|E/hc| \sim 0 \text{ cm}^{-1}$ , superimposed upon a weak narrow impurity pattern. The separation of the outermost lines of the  $\Delta m_s = 1$  region of the **Sd** or **Md** triplet spectrum,  $2D' = 275 \text{ G}$ , was slightly smaller than the corresponding values of 302 G observed for the narrow triplets **Sb** and **Sc** obtained by 345 nm irradiation of the *N*-tosyl- and *N*-brosyl diazenes **5b** and **5c**, but substantially smaller than the 404 G splitting in the **Mb** spectrum obtained from **5b**. The phenyl substituent in <sup>3</sup>**1d** should decrease the zfs (see below), but it is not easy to predict just how much the decrease should be. Therefore, it is not obvious from the splitting alone whether the  $2D' = 275 \text{ G}$  signal from **5d** should be called **Sd** and assigned to a carrier <sup>3</sup>**11d**, structurally similar to the anti diazenyl biradical rotamer <sup>3</sup>**11b**, or **Md** and assigned to <sup>3</sup>**12d**, corresponding to syn rotamer <sup>3</sup>**12b**. At present, we are inclined to favor the first of these alternatives, **Sd**, because the spectrum is stable at 77 K, as is the case with **Sb** but not with **Mb**. The spectrum we now tentatively call **Sd** was accompanied by a weak but observable  $\Delta m_s = 2$  signal at half-field.

**Irradiation of **5d** at 265 nm.** Irradiation of a 77 K glass of diazene **5d** in MTHF at 265 nm for 40 s caused the growth of a strong six-line triplet ESR pattern **Ld** (Figure 3) in the  $\Delta m_s = 1$  region with transitions at 3101, 3192, 3207, 3404, 3423, and 3502 G (microwave frequency = 9.261 GHz) superimposed upon weak impurity resonances in the center of the spectrum. The zfs parameters were  $|D/hc| = 0.0187 \text{ cm}^{-1}$  and  $|E/hc| = 0.0005 \text{ cm}^{-1}$ . A half-field transition was observed at 1647 G. We propose that the carrier of this spectrum is the triplet state of *N*-tosyl-2-phenyl-3,4-dimethylenepyrrole biradical <sup>3</sup>**1d**. Note the decrease in the value of the zfs parameter upon phenyl substitution: <sup>3</sup>**1b**,  $|D/hc| = 0.0226 \text{ cm}^{-1}$ ; <sup>3</sup>**1d**,  $|D/hc| = 0.0187 \text{ cm}^{-1}$ , corresponding to a narrowing of the separation of the

(19) (a) This is an application of a method for generating biradicals developed by Haider, Platz, and co-workers<sup>19b</sup> and used in our laboratory to prepare 3,4-dimethylenethiophene.<sup>19c</sup> (b) Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V. Migirdicyan, E.; Bally, T.; Hasselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318. (c) Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *Ibid.* **1989**, *111*, 3671.





**Figure 3.** ESR spectrum obtained by 265 nm irradiation of diazene **5d** in MTHF at 77 K. The spectrometer microwave frequency is 9.28 GHz. The fields of the resonances are (from left to right) 3101, 3192, 3207, 3404, 3423, and 3502 G; they are superimposed upon weak impurity resonances in the center of the spectrum. A weak  $\Delta m_s = 2$  transition (not shown here) occurs at approximately half-field.

outermost  $\Delta m_s = 1$  lines by about 90 G. This effect is consistent with the structural assignment if the 2-phenyl ring of **31d** can acquire some spin density, thereby decreasing the average propinquity of the unpaired electrons. If the mechanism of spin delocalization involves only the  $\pi$ -electrons, the optimum torsional geometry would require planarity of the phenyl and pyrrole rings. However, it is not obvious that some delocalization by spin polarization cannot also occur. In any case, whatever the geometry, the empirical observations are reminiscent of other diminutions of the  $D$  value by phenyl substitution.<sup>20</sup> Note also that the strong bands of the spectrum each are comprised of two overlapping but discernible transitions. Thus, the value of the zfs parameter  $|E/hc|$  in the spectrum **Ld** of **31d** is finite, which indicates that the accidental degeneracy of two of the triplet sublevels seen in both **31b** and **31c** is lifted by the unsymmetrical phenyl substitution in **31d**.

Like the triplet biradicals **31b** and **31c**, the triplet **31d** was persistent for many hours in the dark at 77 K.

**Is the Long-lived Spin Isomerism a Consequence of Disjoint Character of the Biradicals 1b–d?** The great majority of rate constant measurements for singlet–triplet intersystem crossings (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 values range over about 13 orders of magnitude.<sup>15</sup> Carbonyl  $n, \pi^*$   $S_1$ – $T_1$  crossing typically is characterized by fast rates near  $10^{10}$ – $10^{11}$   $s^{-1}$ , whereas aromatic hydrocarbon  $S_1$ – $T_1$  rates are near  $10^8$   $s^{-1}$ . Excited-to-ground state transitions can be much slower: for benzene- $d_6$ , the  $T_1$ – $S_0$  rate is near  $10^{-2}$   $s^{-1}$  at 77 K. Little is known about the rates of intersystem crossing in systems where the two multiplets are close competitors for the designation of “ground state.” One example of the latter category is the case of the spin isomers studied here, the  $N$ -arenesulfonyl-3,4-dimethylenepyrrole biradicals **1b–d**, which persist for weeks. The rate constants must be  $<10^{-7}$   $s^{-1}$ , and the 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 this additional retardation. The first emerges from the nature of disjoint biradicals. We assume that the only effective intramolecular mechanism mediating isc in these systems is the spin–orbit

interaction.<sup>21,22</sup> In the theory of radiationless transitions,<sup>23</sup> the rate constant for isc is proportional (see eq 1) to a term  $C_{\text{vib}}$ , which incorporates constants and vibronic terms, and to the square of the elements of the coupling matrix which expresses the mixing of the singlet and triplet wave functions by the spin–orbit coupling operator  $H_{\text{so}}$ .

$$k_{\text{isc}} = C_{\text{vib}} \langle T | H_{\text{so}} | S \rangle^2 \quad (1)$$

The non-zero matrix elements have the form of (2):

$$\text{matrix element} = 4NZhbi (\lambda - \sqrt{1 - \lambda^2}) (\zeta_{\text{AB}}^\sigma + \zeta_{\text{AB}}^\pi) \quad (2)$$

As Salem and Rowland have emphasized,<sup>21a</sup> the components of the matrix element have important implications for understanding the structural influences on the rate constant. Thus, the term  $4NZhbi$  expresses the requirement for proper orbital orientation to accommodate the “torque” of the spin flip. Ideally, the transition should occur between orbitals with axes orthogonal to each other and to the axis about which orbital angular momentum is created. The term  $\lambda - (1 - \lambda^2)^{1/2}$  denotes the difference between the coefficients of the two two-electron wave functions<sup>21b</sup> which, in this approximation, are linearly combined to constitute the singlet state; the term  $\zeta_{\text{AB}}^\sigma + \zeta_{\text{AB}}^\pi$  is related to distance/overlap properties of the orbitals involved in the spin-flip.

The term  $\lambda - (1 - \lambda^2)^{1/2}$  defines the ionic character of the singlet state. Physically, the ionic character must be high to facilitate isc, because only if the singlet wave function has contributions from “ionic” configurations, with doubly occupied orbitals, can the spin flip create orbital angular momentum. The extreme cases are (i) a fully ionic state in which  $\lambda = 1$  and the ionic character is unity and (ii) a fully covalent state in which  $\lambda = 1/\sqrt{2} = (1 - \lambda^2)^{1/2}$  and the ionic character is zero. In the latter case, it is immediately clear from eqs 1 and 2 that the matrix element and the rate constant  $k_{\text{isc}}$  will vanish.

Borden and Davidson<sup>24</sup> make the point that because of the separability (near-zero overlap) of the NBMOs of disjoint biradicals, one expects the singlet wave function of these species to have low ionic character. For example, the ionic character of the singlet state wave function of TME **1** is calculated to be about 5%. The rate  $k_{\text{isc}}$  for this molecule is at present experimentally unknown, but it would be expected on the above basis to be retarded relative to some ideal rate by a factor of about  $(1/20)^2 = 1/400$ . When we found the extraordinarily slow rates of isc in biradicals **1b–d**, which are after all TME derivatives, we wondered whether the ionic character of these singlets might be low enough to depress the rate of isc to near zero, and hence whether the long-lived spin isomerism observed

(21) (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) See also: Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3568. This paper refines the earlier approximation<sup>21a</sup> with more accurate wave functions. Qualitatively, the argument we give here persists in the later version of the theory. We thank J. Michl for a discussion of this point. (c) Note that in general hyperfine-induced S–T mixing will make a negligibly small contribution to isc in  $\pi$ -conjugated non-Kekulé biradicals, because it requires that the singlet and triplet energies match to within the energy of the hyperfine interaction (about  $10^{-6}$  kcal/mol). This matching is easily achieved during diffusive radical-pair encounters,<sup>22</sup> but barring an accidentally exact S–T degeneracy, will not occur in static systems such as those in the present work.

(22) Reviewed by: Glarum, S. H. In *Chemically Induced Nuclear Polarization*; Lepley, A. R., Closs, G. L., Eds.; Wiley-Interscience: New York, NY, 1973; Chapter 1.

(23) (a) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962. (b) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187. (c) Jortner, J.; Rice, S. A.; Hochstrasser, R. M. *Adv. Photochem.* **1969**, *7*, 149.

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

(20) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725 and references cited therein.

in these cases might be a dramatic and uniquely characteristic manifestation of their disjoint nature.

Further examination,<sup>25</sup> however, has cooled our enthusiasm for this explanation. A rate constant of about  $10^8 \text{ s}^{-1}$  would be a reasonable estimate of an average value for an idealized  $k_{\text{isc}}$  unretarded by any deficit of ionicity.<sup>15</sup> The observed maximum rates for **1b–d** are slower than that by at least 15 orders of magnitude. To ascribe the latter retardation entirely to low ionic character, it would be necessary that the singlet wave function for **1b–d** be ionic to no more than one part in  $\sqrt{10^{15}}$ , or  $1/(10^{7.5})$ . Conceivably, perturbations by the nitrogen and its attached substituent might reduce the ionic character of the TME singlet from the calculated<sup>24</sup> value of 5% to almost precisely zero in one of the pyrrole derivatives. However, it seems improbable that this accident could recur in four separate molecules: **1b–d** and the 1,3-di-2-pyrrolylbenzene counterpart described in an accompanying paper.<sup>1e</sup> Low ionic character of the singlet wave function may well contribute to the rate retardation, but it would seem that some other feature must be responsible for a major portion of the effect. Accordingly, we have proposed an alternative interpretation.

**Is the Long-lived Spin Isomerism a Consequence of a Conformation-Dependent State Ordering?** The postulate that underlies all of the present work is that a sufficiently strong EWG as a substituent on nitrogen will produce a 3,4-dimethylenepyrrole biradical with a small energy separation between the lowest singlet and triplet. In this narrow span of energies, it seems possible that small structural or conformational changes could alter the energy separation or even interchange the energetic ordering of the multiplet states. Most plausibly, conformational isomerism would be associated with internal rotational orientation about the S–N and S–C bonds of the arenesulfonyl group. Interconversion among conformations could be slow, because of the high viscosity of the matrix and because of one or more finite rotational barriers within the biradical itself. Although no experimental determinations of the rotational barriers in sulfonamides seem to be available, Breneman<sup>29</sup> has used ab initio theory to calculate that the barrier in simple sulfonamides is in the range of 5–9 kcal/mol (gas phase). Thus, even without considering a retardation by the viscosity of the matrix, conformational lifetimes at 77 K or lower temperatures in the present work might be expected to be of the order of at least a few seconds to many centuries. By this means, in a **1b** biradical formed at low temperature in a particular conformation, and hence in a particular spin state, the multiplicity might be effectively frozen.

Under these circumstances, it becomes ambiguous to think of which spin state is energetically preferred unless the conformation is specified. For the present, there is no experimental basis for assigning particular conformations to particular spin states, but in the context of this work, the major idea is that the conformation *determines* the favored spin. Note that *if the triplet–singlet energy gap is small, a conformationally induced change in it of the order of a few tenths of a kcal/mol would suffice to switch the observed multiplicity of the ground state.*

Recent high-level ab initio calculations<sup>26</sup> on the hypothetical model compound *N*-sulfonyl-3,4-dimethylenepyrrole confirm the proposed dependence of the triplet–singlet energy separation on conformation. At the CASSCF (CASPT2N)/6-31G\* level, the gap is smaller by 0.6 (0.8) kcal/mol in the conformation

with the H–S bond of the HSO<sub>2</sub> group perpendicular to the pyrrole ring plane than in the conformation with it in the ring plane. This would be ample to support the proposed conformational spin specificity. At the present stage of refinement, however, the calculations on the model compound do not agree particularly well with the deduction<sup>1</sup> from semiempirical theory that the gap should be very small in the *N*-arenesulfonyl biradicals **1b–d**. The ab initio calculations predict that the absolute value of the smaller gap still should favor the singlet of the HSO<sub>2</sub> model compound by 5.3 (7.2) kcal/mol. Taken at face value, this large a gap would have precluded detection of an ESR triplet signal. That such a signal is nevertheless observed could mean that the gap will narrow on further computational refinement, or that the H–SO<sub>2</sub> substituent is an inadequate model for the ArSO<sub>2</sub> groups we used experimentally, or that the ESR triplet signals we assign to **31b–d** are caused by other presently unknown species. For the moment, we press ahead on the assumption that one (or both) of the first two of these possibilities will prove to be correct.

**Mechanism of the Photodeazetation of Diazene 5b to Triplet Species. Important Common Features of the Mechanisms of Formation and the Properties of the Biradicals 1b–d.** It should be clear that in order to observe the separate kinetically stable singlet and triplet spin states of *N*-arenesulfonyl-3,4-dimethylenepyrrole biradicals, not only must the interconversion of the multiplets be slow, but also, there must be mechanisms for the photolysis of the diazene precursors that give one or the other multiplet specifically in a wavelength-dependent manner. Perhaps the most striking aspect of the observations is the switch from singlet product **11b–d** formed in 370 nm irradiation to triplet product **31b–d** formed in 265 nm irradiation. One plausible explanation involves excitation of the (localized) arenesulfonyl chromophore of diazenes **5b–d**, intersystem crossing to the excited triplet state, and intramolecular transfer of triplet energy to the (localized) diazene chromophore. At present, we have no decisive experimental evidence on these speculations, but the Supporting Information discusses the issue further.

**Search for Thermal Singlet–Triplet Interconversion in Soft Matrices.** To decrease the contribution of the matrix to the overall conformational rotational barrier, thus facilitating interconversion of the spin isomers of biradical **1b**, one needs a matrix significantly less viscous than those used in the studies already described. However, the medium still must be sufficiently viscous to prevent rapid motional averaging<sup>27</sup> of the ESR anisotropic interactions and permit observation of the triplet transitions. We have photolyzed the *N*-tosyl diazene precursor **5b** in a 2:3 (v/v) mixture of 1- and 2-propanols. This medium previously has been shown in this laboratory<sup>27b</sup> to support the characteristic ESR spectrum of the TMM biradical 2-isopropylidencyclopentane-1,3-diyI at temperatures as high as 143.6 K, where its viscosity  $\eta \sim 2000 \text{ P}$ .<sup>28</sup> Under these conditions, and even at temperatures down to 120.8 K, the biradical's mobility is sufficient to permit observation of its dimerization kinetics and intermolecular capture by acrylonitrile on a convenient time scale.

Although we have now observed what seem to be definite motional effects on the zfs parameter  $|D/hc|$  in these and other matrices containing **31b** or other triplet species (see the Supporting Information), we find no evidence for thermal interconversion of the singlet and triplet states of **1b** in propanol

(25) We are grateful to Professors Salem, Borden, and Davidson, whose unanimous resistance to this idea forced us to examine its implications more closely.

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

(27) (a) Weissman, S. A. *J. Chem. Phys.* **1958**, *29*, 1189. (b) Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358.

(28) Greenspan, H.; Fischer, E. *J. Phys. Chem.* **1965**, *69*, 2466.

(29) Breneman, C. M.; Weber, L. W. *Can. J. Chem.* **1996**, *74*, 1271. We thank C. M. Breneman for providing this information before publication.

matrices so far. The triplet signal persists up to about 90 K, but no blue color is visible. Similarly, blue samples of **1b** singlet at temperatures up to 90 K do not show the characteristic ESR resonances of triplet **1b**. Since the blue samples generated in propanols usually contain one or both of the diazenyl triplets **11b** and **12b**, the latter experiment also serves to show that thermal deazetation of the diazenyl biradicals, a reaction that might have given the **1b** triplet, does not occur in this medium. This result resembles the findings already described in MTHF glasses.

**Conclusions.** Both the singlet and the triplet states of the three *N*-arenesulfonyl-3,4-dimethylenepyrrole biradicals **1b–d** can be prepared in glassy matrices. They are individually kinetically stable for many days and thus constitute examples of long-lived spin isomerism. The intersystem crossings are at least 15 orders of magnitude slower than those of typical triplet–singlet pairs. The most plausible current explanation for this retardation is that the molecular conformation in **1b–d** determines which spin state is energetically preferred. Intersystem crossing then must be coupled to conformational isomerization about the N–S and/or S–C bonds of the biradicals, which can be a very slow process at low temperatures.

Conformational control of the ground state multiplicity is a delicate indirect effect. It depends upon the circumstance that conformational isomerization<sup>30</sup> alters the singlet–triplet energy gap by a small but finite amount (computationally<sup>26</sup> less than 1 kcal/mol). In order for such control to operate as proposed for the present examples, the energies of the triplet and singlet must be nearly the same. This would be in accord with the computationally based prediction<sup>1a,c</sup> that a sufficiently EW *N*-substituent will damp the heteroatom lone-pair perturbation in a 3,4-dimethylenepyrrole and restore the multiplets to the near-degeneracy characteristic of the disjoint hydrocarbon TME.

## Experimental Section

Photochemical, UV–vis spectroscopic, and solvent purification techniques were similar to those described earlier.<sup>1a,5e,6a</sup> ESR spectroscopic procedures and methods for the AM1-CI calculations are given in the Supporting Information to our preliminary communication.<sup>1a</sup>

**Synthesis of Precursor 5d (Scheme 1).** **2-Phenyl-3,4-bis(methoxymethyl)-*N*-*p*-toluenesulfonylpyrrole (9)**. 2-(Trimethylstannyl)-3,4-bis(methoxymethyl)-*N*-*p*-toluenesulfonylpyrrole (**8**)<sup>1d</sup> (1.96 g, 4.16 mmol) and bis(acetonitrile)–palladium dichloride (0.1 g, 0.386 mmol) were added to a 25 mL round bottom flask, which was then evacuated and flushed with argon three times. To this was added iodobenzene (0.38 mL, 3.40 mmol), followed by 10 mL of anhydrous 2-methyl-1-pyrrolidinone.

The mixture was stirred under argon for 16 h at room temperature. After standard workup, the crude product was purified by column chromatography (silica gel, 1:4 ethyl acetate/hexanes) to yield a clear oil (0.384 g, 29%): <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.41 (s, 1H), 7.34–7.26 (m, 4H), 7.18–7.01 (m, 5H), 4.38 (s, 2H), 3.98 (s, 2H), 3.36 (s, 3H), 3.11 (s, 3H), 2.29 (s, 3H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>) δ 144.56, 135.41, 133.93, 131.85, 129.32, 129.20, 128.40, 127.13, 127.08, 123.29, 121.09, 66.42, 64.95, 57.98, 57.50, 21.31; D/EI (20 eV) *m/z* 385 (M<sup>+</sup>, 28%), 354 (M<sup>+</sup> – OMe, 6%), 323 (M<sup>+</sup> – 2OMe, 4%), 198 (M<sup>+</sup> – Ts – MeOH, 100%).

**2-Phenyl-3,4-bis(bromomethyl)-*N*-*p*-toluenesulfonylpyrrole (21)**. A suspension of the above crude compound **9** (0.366 g, 0.951 mmol), dibromotriphenylphosphorane (1.07 g, 2.43 mmol), and acetonitrile (15 mL) was brought to reflux for 5 h. After cooling to room temperature, the mixture was poured into saturated sodium bicarbonate solution (30 mL). This was extracted with ether (4 × 30 mL). The ether layers were combined, washed with water (50 mL), dried over MgSO<sub>4</sub>, and

concentrated. Purification was achieved by column chromatography (silica gel, 1:9 ethyl acetate/hexanes) gave a white solid (0.263 g, 57%): mp 120–122 °C; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.52 (s, 1H), 7.43–7.28 (m, 4H), 7.19–7.07 (m, 5H), 4.55 (s, 2H), 4.21 (s, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>) δ 145.22, 134.96, 134.31, 131.46, 129.49, 129.15, 128.34, 127.59, 127.38, 122.78, 122.31, 121.64, 23.85, 21.54; D/EI (20 eV) *m/z* 485 (M<sup>+</sup> + 4, 15%), 483 (M<sup>+</sup> + 2, 27%), 481 (M<sup>+</sup>, 14%), 404 (M<sup>+</sup> + 2 – Br, 64%), 402 (M<sup>+</sup> – Br, 59%), 323 (M<sup>+</sup> – 2Br, 14%), 168 (M<sup>+</sup> – Ts – 2Br, 100%).

**1',2',3',4'-Tetrahydro-2',3'-di-*tert*-butoxycarbonyl-5'-phenyl-6'-*p*-toluenesulfonylpyrrolo[3,4-*d*]pyridazine (10)**. A mixture of potassium *tert*-butoxide (0.157 g, 1.33 mmol), 18-crown-6 (0.064 g, 0.242 mmol), di-*tert*-butylhydrazine dicarboxylate (0.137 g, 0.590 mmol) in 16 mL of THF was heated to reflux for 1.5 h. To this was slowly added the above dibromide (0.285 g, 0.590 mmol) in 8 mL of THF. The reaction mixture was brought to reflux for another 9 h. After workup, a brownish orange oil was obtained. The crude product was purified by column chromatography (silica gel, 1:2 ether/hexanes) to yield pale yellow solids (0.194 g, 59%). NMR showed that two conformers were present: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.31–7.08 (m, 10H), 5.08 (bd. d, *J* = 15 Hz, 1H), 4.88 (minor conformer, bd. d, *J* = 15 Hz), 4.72 (bd. d, *J* = 15 Hz, 1H), 4.47 (minor conformer, bd. d, *J* = 15 Hz), 4.23 (minor conformer, bd. d, *J* = 15 Hz), 4.11 (bd. d, *J* = 15 Hz, 1H), 3.97 (minor conformer, bd. d, *J* = 15 Hz), 3.87 (bd. d, *J* = 15 Hz, 1H), 2.34 (s, 3H), 1.42 (s, 18H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 154.3, 144.84, 35.52, 131.11, 129.50, 128.58, 127.71, 127.27, 120.29, 118.65, 117.20, 81.27, 41.11, 42.70 (minor conformer), 41.26 (minor conformer), 40.92, 28.30, 28.20, 21.65; D/EI (20 eV) *m/z* 553 (M<sup>+</sup>, 3%), 397 (M<sup>+</sup> – TsH, 28%), 242 (M<sup>+</sup> – Ts – CO<sub>2</sub>Bu – <sup>t</sup>Bu + H<sub>2</sub>, 84%), 57 (<sup>t</sup>Bu, 100%); HRMS (FAB) calcd for C<sub>29</sub>H<sub>35</sub>N<sub>3</sub>O<sub>6</sub>S(Na<sup>+</sup>) 576.2144, found 576.2143.

**1',2',3',4'-Tetrahydro-5'-phenyl-6'-*p*-toluenesulfonylpyrrolo[3,4-*d*]pyridazine**. The hydrazine was generated from biscarbamate **10** in the same manner as described for corresponding transformations in the accompanying paper:<sup>1c</sup> <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.32–7.10 (m, 10H), 3.98 (s, 2H), 3.69 (s, 2H), 2.34 (s, 3H).

**1',4'-Dihydro-5'-phenyl-6'-*p*-toluenesulfonylpyrrolo[3,4-*d*]pyridazine (5d)**. Diazene **5d** was obtained by DMAD oxidation of the hydrazine at –30 °C using the same procedure as described for similar transformations.<sup>1c</sup>

**Test for Equilibration of the Triplet and Singlet Biradicals <sup>3</sup>1b and <sup>1</sup>1b as the Cause of the Slight Curvature in the Curie Law Plots.** We observed that a 0.005 M sample of tosyl diazene **5b**, when photolyzed at 370 nm for 20–30 min appears blue. At 77 K no hint of ESR signal attributable to <sup>3</sup>1b was observed. Assuming, quite conservatively, that only a volume of 50 μL of the sample is actually “read” and that the total amount of diyl is only 5% of the initial diazene concentration, as is suggested by the diminution of the UV–vis absorption:

$$0.005 \text{ M (50 } \mu\text{L)} = 2.5 \times 10^{-7} \text{ mol of diazene in cavity}$$

$$2.5 \times 10^{-7} \text{ mol of diazene (5\% diazene to diyl)} =$$

$$1.25 \times 10^{-8} \text{ mol of diyl in cavity}$$

$$1.25 \times 10^{-8} \text{ mol of diyl (6.02} \times 10^{23} \text{ molecules/mol)} =$$

$$7.5 \times 10^{15} \text{ molecules of diyl}$$

The fraction of triplet is governed by the Boltzmann distribution. For a gap of 19 cal/mol,

$$f_{\text{triplet}} = \frac{3e^{(-\Delta E/RT)}}{1 + 3e^{(-\Delta E/RT)}} = \frac{3e^{(-19/1.99(77))}}{1 + 3e^{(-19/1.99(77))}} = 0.73$$

Now we calculate the number of spins which should be present:

$$7.5 \times 10^{15} (73\%) = 5.5 \times 10^{15}$$

$$\text{two spins per triplet biradical} = 1.1 \times 10^{16} \text{ spins}$$

This extremely conservative value is still 1 order of magnitude greater

(30) Although not mediated by internal rotational conformation, spin isomerism has been observed in transition metal complexes. Review: Gütllich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024.

than the nanomolar detection limit of the instrument. We conclude, therefore, that either the triplet  $^3\mathbf{1b}$  is not in rapid equilibrium with anything, or if it is then it is *not* with the blue species  $^1\mathbf{1b}$ .

**Synthesis of the Rearranged Bis-carbamate 1',2',3',4'-Tetrahydro-2',3'-dicarbomethoxy-5'-p-toluenesulfonylpyrrolo[3,4-d]-pyridazine 19 by Photo-Fries Rearrangement of 18.** The *N*-tosyl bis methyl carbamate **18** has been reported elsewhere<sup>6a</sup> and was prepared in the present work by methods described<sup>1c</sup> for the synthesis of the corresponding bis di-*tert*-butylcarbamate. The  $^1\text{H}$  NMR spectrum matched that found previously.<sup>6a</sup> Irradiation of the *N*-tosyl bis-carbamate **18** in solution in benzene, acetonitrile, THF, MTHF, or methanol with the 1000 W Hg–Xe arc either unfiltered or NiSO<sub>4</sub>-filtered gave the rearranged bis-carbamate **19** as product, together with a small amount of starting material. In some of the solvents, traces of the detosylated bis-carbamate were observed. In a specific run, a solution of 30 mg of **18** in 2 mL of methanol was irradiated without filter for 50 min under a N<sub>2</sub> atmosphere at room temperature. The solvent was evaporated, and the dark brown residue was chromatographed on silica gel with 50% EtOAc in pentane to give 6 mg (20%) of the rearranged bis-carbamate **19**. With NiSO<sub>4</sub>, the same product again was observed, but the yield was lower. Under 366 nm irradiation, no rearranged product was observed:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$ /ppm 9.9 (1H, bs), 7.77 (2H, d  $J$  = 8.3 Hz), 7.28 (2H, d  $J$  = 8.3 Hz), 6.76 (1H, d  $J$  = 2.5 Hz), 5.32–4.32 (4H, m), 3.75 (3H, s), 3.74 (3H, s), 2.40 (3H, s); HRMS (CI) calcd for C<sub>17</sub>H<sub>20</sub>N<sub>3</sub>O<sub>6</sub>S (M + 1) 394.107282, found 394.108368.

**Solution Phase Direct Photolysis of Diazene 5b by NiSO<sub>4</sub>-Filtered Light in the Presence of Maleonitrile (MN).** A sample of diazene compound **5b**<sup>1a-c</sup> (2 mL, 15 mM) and maleonitrile (0.032 mmol, 0.4 mL, 0.08 M) in 2-MTHF was degassed and sealed in a square quartz tube equipped with a Pyrex extension. The sample was photolyzed with NiSO<sub>4</sub>-filtered light for 30 min at –40 °C. It was then treated with *N*-methylmaleimide (NMM) (0.875 mL, 1 M) and allowed to warm to room temperature to scavenge any unreacted diazene.<sup>1c</sup> HPLC analysis (20% EtOAc in hexane) showed no detectable product. Apparently the products of the reaction are very unstable under these reaction conditions. This was confirmed by separate control experiments, which showed efficient photodecomposition of maleonitrilediyl **1b** adducts under these conditions.

**Direct Photolyses of Diazene 5b. Extent of Deazetation by 265 nm, 343 nm, 366 nm, and NiSO<sub>4</sub>-Filtered Light by UV–Vis Spectroscopy.** These experiments were designed to monitor the extent of deazetation in *N*-tosyl diazene **5b** at 77 K using different filters. The sample of azo compound **5b** (15 mM solution in MTHF) was irradiated at 265 or 343 nm monochromatic light at 77 K for 100 min total time. The wavelengths were selected by means of an Oriel 7725 monochromator. Comparison of the UV spectra of the sample after 100 min total irradiation with the spectra prior to irradiation showed no change.

Irradiation by (mostly) 366 nm light (passed by Oriel colored glass filter of peak transmission 328–381 nm) of *N*-Tos diazene **5b** at 77 K for 13 min total irradiation showed 28.8% decrease of the 370 nm band in the spectrum.

**Table 3.** Product Ratios from the Experiments of Scheme 4

time, min	relative % DMAD Product <b>18</b>	relative % NMM Product <b>20</b>
15	22	78
30	30	70
60	50–58	50–42

Irradiation with NiSO<sub>4</sub>-filtered light (1 M aqueous NiSO<sub>4</sub>, peak transmission 230–325 nm) gave some change in the spectrum, including new bands at ~390 and ~360 nm, which made difficult an estimate of how much the 370 nm band decreased.

**Direct Photolyses of *N*-Tosyl Diazene 5b with 265 nm, 366 nm, and NiSO<sub>4</sub>-Filtered Light in MTHF Matrix Containing DMAD.** Three samples of diazene **5b** (1 mL, 15 mM) in 2-MTHF and DMAD (4 mg, 0.02 mmol) were sealed in the standard way in square quartz tubes. One sample was photolyzed at 77 K at 265 nm for 20 min; another at 366 nm for 15 min; the third with NiSO<sub>4</sub>-filtered light for 15 min. Each sample was then allowed to warm to room temperature in the dark. The products were analyzed by  $^1\text{H}$ -NMR in CDCl<sub>3</sub>. The only trapping product observed was the fused *N*-tosyl bis-carbamate **18**. The spectrum also showed no growth of the rearranged 2-tosyl bis-carbamate **19**.

In another experiment (Scheme 4), a sample of diazene **5b** (0.7 mL, 8.5 mM) in 2-MTHF and DMAD (20.43 mM) was placed in a capped square quartz tube and purged with nitrogen. Three samples were photolyzed by NiSO<sub>4</sub>-filtered light at 77 K for 15, 30, and 60 min, respectively. After irradiation the tubes were stored at –80 °C, and *N*-methylmaleimide (0.5 mL, 1 M) was added to scavenge unreacted diazene. The samples then were allowed to warm to room temperature in the dark. The products were analyzed by HPLC using 40% EtOAc/hexane as a solvent system. The product peaks were assigned by comparison to pure samples. The comparison of three runs (Table 3) showed relative growth of trapping product *N*-tosyl bis-carbamate **18** with increasing reaction time, and relative decrease of the *N*-Me maleimide trapped product **20**. The HPLC chromatograms also showed the absence (<0.1%) of the rearranged 2-tosyl bis-carbamate **19** in the crude photolysis product.

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**Supporting Information Available:** Curie Law, spin-count, and temperature-dependent ESR zero-field splitting experiments (37 pages). See any current masthead page for ordering and Internet access instructions.

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