Laser Flash Photolysis of Dithio-2,2′-dipyridine; Structure and Reactivity of Pyridyl-2-thio Radical

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Photochemical reactions of dithio-2,2′-dipyridine were studied by the laser flash photolysis method to clarify the structure and reactivities of the intermediate radical. The transient absorption band appearing at 490 nm was attributed to a radical in which the unpaired electron was mainly localized at the sulfur atom, namely, pyridyl-2-thio radical (2-PyS˙). The low reactivities of 2-PyS˙ to O_2 and hydrogen-atom donors were confirmed by the invariance of the decay rates of 2-PyS˙. The high reactivity of 2-PyS˙ in addition reactions to conjugated dienes was confirmed by the accelerated first-order decay rate of 2-PyS˙ upon addition of the diene. For example, the addition reaction rate constant for isoprene was 1.2×10^9 M^{-1} s^{-1} (in THF), which is higher than that of PhS˙. Such reactivities were interpreted by comparison with MO calculations.

Introduction

It was reported by Bohne, Boch, and Scaiano that the transient absorption band of pyridyl-2-thio radical (2-PyS˙) is observed at 485 nm upon laser flash photolysis of *N*-hydroxypyridine-2-thione esters (**1** in Scheme 1).[1] This photolysis has been used in a radical chain reaction for synthetic purposes by Barton et al.[2,3] Newcomb et al. used the esters as radical precursors in kinetic studies and measured various rate constants for radical reactions.[4,5] Although the radical primarily produced from the photolysis of **1** is N-centered radical **2**, the 485 nm band was assigned to the S-centered radical **3** due to its similarity to the absorption peak of arylthio radicals (ArS˙).[6–10] We report here the transient spectra observed by laser photolysis of dithio-2,2′-dipyridine (**4** in Scheme 2) and its derivative. Comparison of the reactivities of the transient species with those of PhS˙ affords strong evidence for the structure of the radical. We have also examined the question of whether the intermediate radical is S-centered radical **3** or N-centered radical **2** (Schemes 1 and 2) by MO calculation.

Results and Discussion

The transient absorption spectrum observed by laser flash photolysis of disulfide **4** in degassed THF with 266 nm light shows a peak at 490 nm with a tail of a shorter wavelength band (Figure 1). The absorption intensity of the 490 nm band decreases homogeneously with time as shown in Figure 1's inserted time profile, indicating the formation of a single transient species in the region of 400–550 nm. The reported transient absorption band from the laser flash photolysis of thioesters **1** in cyclohexane occurs at 485 nm (Scheme 1),[1] which is quite similar to that from disulfide **4**. This finding indicates that a similar radical is formed from the two different cleavages.

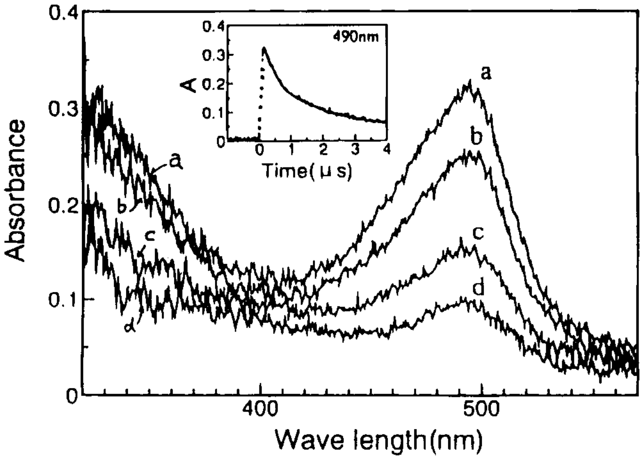
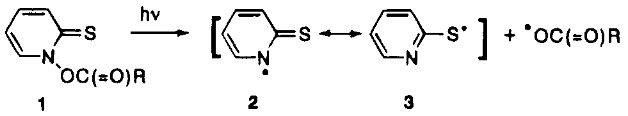
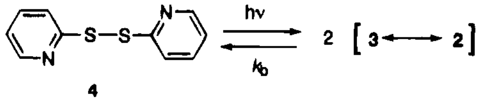


Figure 1. Transient absorption spectra obtained by laser photolysis (266 nm) of dithio-2,2′-dipyridine (**4**, 1 mM) in THF in degassed solution; (a) 50 ns, (b) 300 ns, (c) 1 μs, and (d) 2 μs. Insert: Decay curve at 490 nm.

Scheme 1



Scheme 2



The tail of a transient absorption band whose peak may be at a wavelength shorter than 350 nm also appears. This band is not attributed to the same species as the 490 nm band, because the time profile is different as indicated by the irregular change in absorption intensity with time in the region of 330–400 nm in Figure 1.

The transient absorption spectra observed by the photolysis of disulfide **4** in polar and nonpolar solvents are shown in Figure 2. A slight bathochromic shift of

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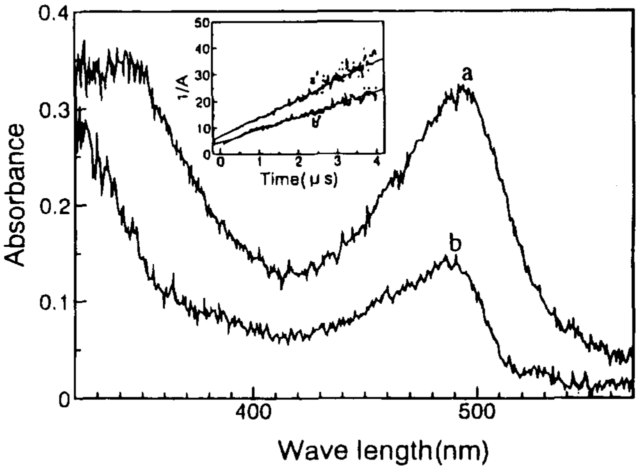
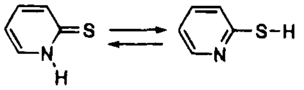


Figure 2. Transient absorption spectra obtained by laser photolysis (266 nm) of dithio-2,2′-dipyridine (**4**, 1 mM) in (a) acetonitrile and (b) cyclohexane. Insert: Second-order plots for the decay of 490 nm band in (a′) acetonitrile and (b′) cyclohexane.

Scheme 3



5 **6**

the absorption peak near 490 nm was observed in polar solvents such as acetonitrile. A large increase in the initial intensity of the transient absorption band was also observed in polar solvents. This suggests a slight change in the distribution of the unpaired electron in the radical; there may be a solvent polarity effect on the relative contributions of the N-centered radical **2** and S-centered radical **3** resonance structures.

In acetonitrile, there appeared an absorption band in the 350 nm region that did not decay within a few microseconds. This band may be attributable to the *N*-hydropyridine-2-thione (**5**), which is a tautomer of 2-mercaptopyridine (**6**) as shown in Scheme 3. In polar solvents, thione **5** predominates over thiol **6**.[11]

In 2-propanol, the spectrum at 480 nm becomes broadened, suggesting some interactions between 2-PyS$^\cdot$ and the solvent.

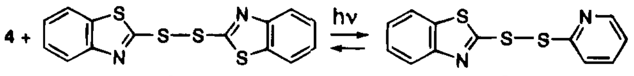
As shown in inserted second-order plots in Figure 2, the radical decays mainly by a recombination reaction into the corresponding disulfide. In acetonitrile, a small amount of the radical may be converted into a 350 nm band species, probably thione **5**, via hydrogen abstraction from solvent. From the slope of the second-order plot, the ratios of the recombination rate constants (k_b in Scheme 2) to the molar extinction coefficients (ϵ) were obtained. They are summarized in Table 1 for various solvents. Since the observed $2k_b/\epsilon$ values depend upon the viscosity (η) of the solvent, the recombination reaction may be close to the diffusion controlled limit (k_d). The k_d value in THF was calculated to be 1.1×10^{10} M^{-1} s^{-1} from the Debye equation ($k_d = 8RT/3000\eta$).[12] Thus, the ϵ value at 490 nm was determined to be ca. 3000 M^{-1} cm^{-1}, from which the initial concentration of 2-PyS$^\cdot$ was calculated to be ca. 0.1 mM (Figure 1). Thus, by one laser exposure of 1 mM disulfide solution, ca. 5% of **4** may be photocleaved under our experimental conditions. In most cases, the decay rate was not affected by the addition of O_2 into the solution. The reactivity of 2-PyS$^\cdot$ to O_2 is low, which is one of the characteristics of the arylthio radicals.[13]

Table 1. Absorption Maxima and Second-Order Decay Kinetics of 2-PyS$^\cdot$

solvent	λ_{max} $(A_0)^a$, nm	$2k_b/\epsilon$, cm s^{-1}	k_d,^{b} M^{-1} s^{-1}	ϵ, M^{-1} cm^{-1}
n-hexane	480 (0.08)	1.5×10^7	2.1×10^{10}	2800
cyclohexane	485 (0.22)	5.0×10^6	6.8×10^9	2700
ethanol	500 (0.22)	8.6×10^6	5.6×10^9	1300
2-propanol	480 (0.14)	8.0×10^6	2.0×10^8	500
THF	490 (0.17)	9.4×10^6	1.2×10^{10}	2600
acetonitrile	495 (0.40	1.2×10^7	1.9×10^{10}	3200

[a] Initial absorbance at absorption maximum when 1 mM solution of **4** was laser photolyzed with a constant power. [b] Diffusion controlled rate constants.

Scheme 4



7 **8**

In 2-propanol, the 485 nm-band decays in second-order kinetics, suggesting a low hydrogen-abstraction reactivity for 2-PyS$^\cdot$. In Table 1, however, the calculated ϵ value in 2-propanol is much smaller than in other solvents. This is due to the faster decay rate than expected, based upon k_d. The hydrogen abstraction reaction may be included in the observed decay rate in 2-propanol, although it keeps second-order kinetics.

In order to confirm the assignment of the radical species, disulfide **8** was produced by the steady-light photolysis of a mixture of disulfide **4** and dithio-2,2′-dibenzothiazole (**7**) as shown in Scheme 4. The benzothiazolyl-2-thio radical (**9**) was selected because the transient absorption is well known and there is no appreciable absorption in the 400–500 nm region.[14]

From laser flash photolysis of disulfide **8**, two transient absorption bands were observed at 490 and 590 nm as shown in Figure 3. The transient absorption band at 590 nm was attributed to the thio radical **9**.[14,15] Thus, this spectrum indicates that the photodissociation occured at the S–S bond as shown in Scheme 5. Each decay showed second-order kinetics suggesting that the thio radicals **3** and **9** decay by a radical coupling reaction into disulfides **4**, **7** and **8**.

After photolysis of disulfide **4** with steady light longer than 270 nm (Xe-lamp) or with 266 nm pulsed laser light in 2-propanol, new absorption bands appeared at 385 and 295 nm, which can be attributed to thione **5**, along with the decrease of the absorption bands of disulfide **4** at 285 and 240 nm (Figure 4). The presumed reaction is shown in Scheme 6. Although this seems to suggest the formation of N-centered radical **2** by the photodissociation of disulfide **4**, the observed kinetic data obtained from the decay of transient bands does not support N-centered radical **2** as the primarily formed radical from disulfide **4**.

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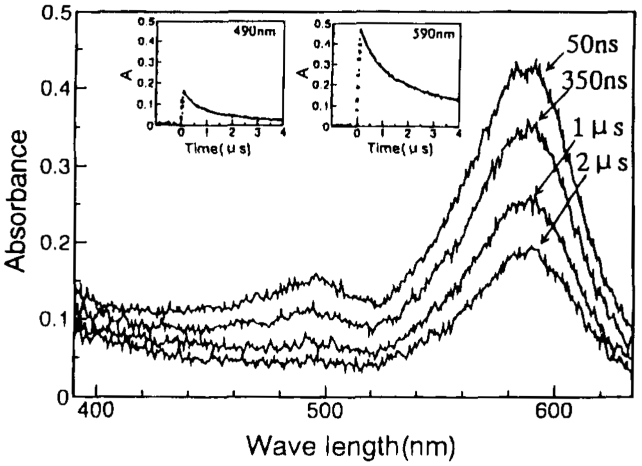


Figure 3. Transient absorption spectra obtained by laser photolysis (266 nm) of disulfide **8** (1 mM) in degassed THF. Insert: Decay curves at 490 and 590 nm.

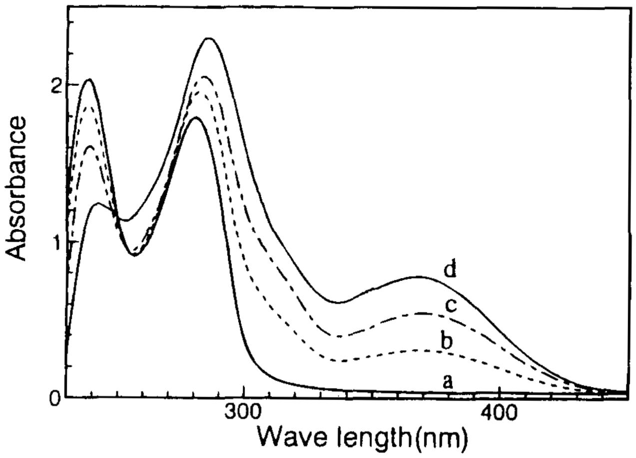
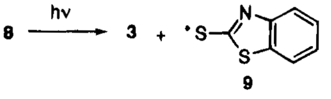
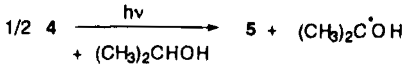


Figure 4. UV spectral changes by steady-light photolysis of dithio-2,2′-dipyridine (**4**, 0.1 mM) with Xe-lamp light longer than 270 nm in 2-propanol in degassed solution; (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min. Spectrum d is same as the spectrum of thione **5**.

Scheme 5



Scheme 6



$$\frac{1}{2}\,\mathbf{4} \xrightarrow[+\ (CH_3)_2CHOH]{h\nu} \mathbf{5} + (CH_3)_2\dot{C}OH$$

Assuming that thio radical **3** is primarily formed from photocleavage of disulfide **4** and that the S-centered radical abstracts the hydrogen slowly from solvent, the appearance of the thione absorption in Figure 4 may be the result of tautomerism of thiol **6** to thione **5** as shown in route a of Scheme 7.

Otherwise, if N-centered radical **2** predominates in polar solvents after the initial S–S cleavage of disulfide **4** (in analogy to the hydrogen-adduct in Scheme 3), the hydrogen abstraction might occur from N-centered radical **2** (route b of Scheme 7). Although we could not obtain evidence to distinguish between the two routes experimentally, the low hydrogen-abstraction ability of 2-PyS$^{\cdot}$ suggests that route a may be preferred.

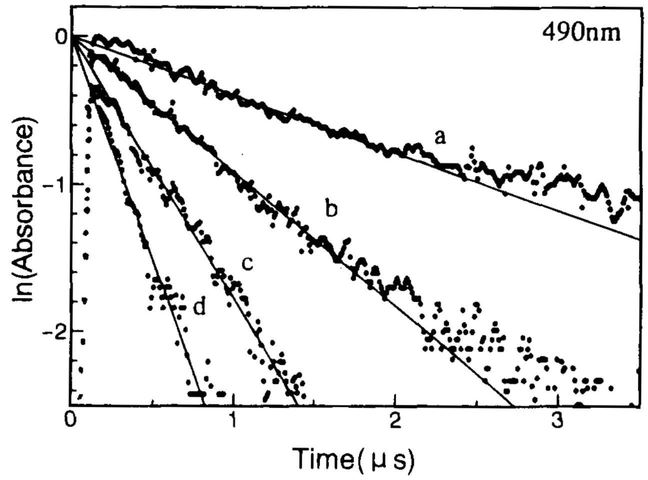
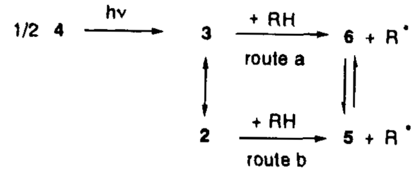


Figure 5. The first-order decay plots of the transient absorption intensity at 490 nm in the presence of isoprene in deaerated THF solution; (a) 0 mM, (b) 1 mM, (c) 2 mM and (d) 3 mM.

Scheme 7



By introducting air into the 2-propanol solution, the appearance of the thione absorption band was suppressed. Although this seems to indicate that radicals **2** or **3** may react with O_2, this interpretation is not in agreement with our finding that the decay profile of the radical (**2** and/or **3**) was not influenced by the presence of O_2 in the time scale of 10 μs. Therefore, the suppression may be attributed to the photo-reaction of thione **5** with O_2; we observed that thione **5** disappears by photoillumination in the presence of O_2.

Addition of isoprene to the solution changes the decay kinetics of the 490 nm band from second-order to first-order as confirmed by the good linearity of the first-order plots (Figure 5). The first-order rate constants (k_{1st}) were evaluated from the slopes, which increase with the concentration of isoprene.

The k_{1st} values thus obtained were plotted against the diene concentration as shown in Figure 6. From the slope of the pseudo-first order plots, the second-order rate constants (k_1) were obtained. The k_1 values for several dienes and for isoprene in other solvents are summarized in Table 2 with the reported rate constants for the reaction of PhS$^{\cdot}$.[16] The rate constants thus obtained for 2-PyS$^{\cdot}$ in a degassed solution are similar to those in a deaerated solution, suggesting that the addition reaction occurs in an irreversible fashion in the presence of excess diene on the time scale of a few microseconds, as employed in this study.

In the presence of 1,4-cyclohexadiene, which has four highly reactive hydrogens, the decay of 2-PyS$^{\cdot}$ was only slightly accelerated. The rate constant is less than ca. 10^7 M^{-1} s^{-1}, which is ca. 1/20–ca. 1/200 of those for conjugated dienes, indicating that hydrogen abstraction by 2-PyS$^{\cdot}$ is slower than its addition to dienes. The low

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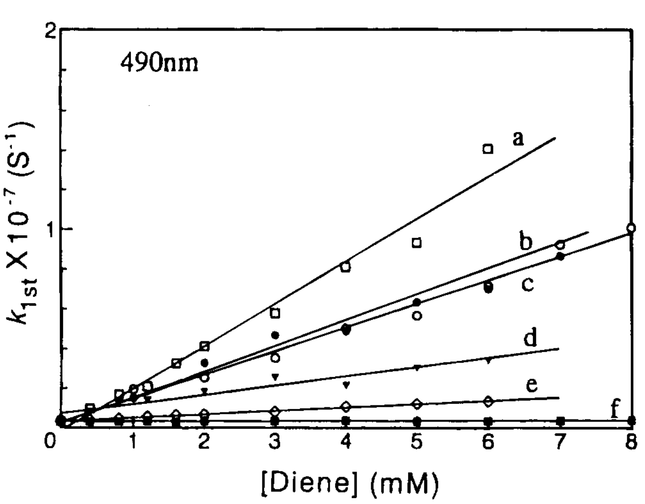


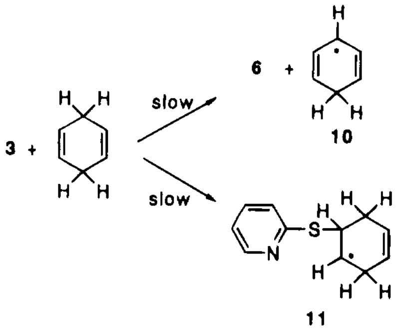
Figure 6. Pseudo-first order plots in deaerated THF except b; (a) 2,3-dimethyl-1,3-butadiene, (b) isoprene in aerated THF, (c) isoprene, (d) 1,4-dimethyl-1,3-butadiene, (e) 1-methyl-1,3-butadiene, and (f) 1,4-cyclohexadiene.

Table 2. Rate Constants (k_1) for the Reactions of 2-PyS$^\cdot$ and PhS$^\cdot$ with Various Dienes at 23 °C in THF

diene	2-PyS$^\cdot$ k_1, M^{-1} $s^{-1\,a}$	PhS$^\cdot$ k_1, M^{-1} $s^{-1\,b}$
2-methyl-1,3-butadiene	1.2×10^9	4.7×10^7
(in cyclohexane	2.0×10^9)	
(in acetonitrile	1.3×10^9)	
2,3-dimethyl-1,3-butadiene	2.1×10^9	9.0×10^7
1-methyl-1,3-butadiene	1.7×10^8	2.0×10^7
1,4-dimethyl-1,3-butadiene	4.7×10^8	2.2×10^7
1,4-cyclohexadiene	($<8 \times 10^6$)	

[a] Each value may contain the experimental error of ±5%. [b] In cyclohexane (ref 16).

Scheme 8



reactivity of 1,4-cyclohexadiene also shows that the addition of 2-PyS$^\cdot$ to nonconjugated double bonds is quite slow (Scheme 8).

On the other hand, the high reactivity to isoprene may be due to the high addition reactivity of 2-PyS$^\cdot$ to conjugated dienes, rather than to hydrogen abstraction from the methyl group of isoprene, although three carbon-centered radicals (**12**−**14** in Scheme 9) are resonance stabilized allyl-type radicals. The formation of a S−C bond giving an allyl-type radical **14** was indicated by the lack of an absorption band in the 300−400 nm region due to thione derivatives like **13**.

For most of the dienes in Table 2, the reactivities of 2-PyS$^\cdot$ are higher than those of PhS$^\cdot$ by a factor of ca. 20. The trend of reactivities of 2-PyS$^\cdot$ toward various dienes is similar to that of PhS$^\cdot$. Terminal methyl substitution suppresses the reaction rate indicating that the addition reaction occurs predominantly at the terminal double bond, producing a resonance stablized allyl-type radical. A central methyl group increases the reactivity of a diene through hyperconjugation.

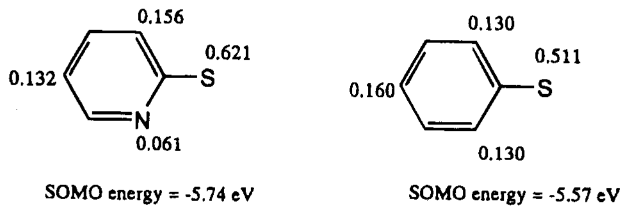
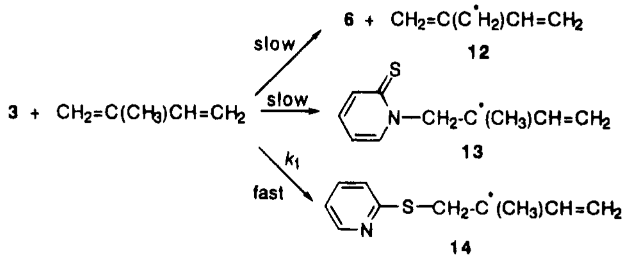


Figure 7. SOMO energy level and the unpaired π-electron density of SOMO of 2-PyS$^\cdot$ and PhS$^\cdot$.

Scheme 9



As shown in Table 2, the addition reaction rate constant of 2-PyS$^\cdot$ to isoprene in cyclohexane is greater than in polar solvents such as THF and acetonitrile by a factor of ca. 2. Although the difference is greater than experimental error, it is not as large as expected from the change in the transient spectra in Figures 1 and 2. These spectroscopic and kinetic data obtained in this study support the S-centered radical **3** as the radical produced from disulfide **4**.

In order to confirm the S-centered radical structure of 2-PyS$^\cdot$, MO calculations were performed. At first, we did the calculation of neutral molecules of thione **5** and thiol **6** by the MNDO method (MOPAC '93).[17,18] The calculated total energy and electronic energy are quite similar for thione **5** and thiol **6**, suggesting easy tautomerization. The dipole moments of **5** and **6** are 6.47 and 2.32 Debye, respectively, confirming the experimental result that thione **5** predominates over thiol **6** in polar solvent.[11]

The unpaired π-electron densities of 2-PyS$^\cdot$ and PhS$^\cdot$ of SOMO calculated by MNDO method are shown in Figure 7. For SOMO of 2-PyS$^\cdot$, the unpaired π-electron density on the sulfur atom is greater than on the nitrogen atom, which confirms our conclusion based on the kinetic considerations. On comparison with PhS$^\cdot$, the unpaired π-electron density on the sulfur atom is higher for 2-PyS$^\cdot$ than PhS$^\cdot$. The observed higher reactivity of 2-PyS$^\cdot$ can be reasonably attributed to the localization of the unpaired π-electron on the sulfur atom. In addition, the SOMO energy calculated for 2-PyS$^\cdot$ is lower than that of PhS$^\cdot$. This suggests that the electrophilicity of 2-PyS$^\cdot$ is higher than PhS$^\cdot$. In the transition state, it would be anticipated that the higher the electrophilicity, the higher the reactivity, since the charge-transfer from diene to radical center may be operative. This also supports the higher reactivity of 2-PyS$^\cdot$ than PhS$^\cdot$. The electronic transition energies for 2-PyS$^\cdot$ and PhS$^\cdot$ were calculated by the restricted Hartree−Fock method with configuration interactions to be 422 and 486 nm, respectively, for the first allowed transition. The calculated λ_{max} for PhS$^\cdot$

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(18) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10* , 209.

is in good agreement with the observed λ_{max} at 490 nm. In the case of 2-PyS$^{\cdot}$, however, the calculated λ_{max} is at considerably shorter wavelength than that observed, suggesting that it is necessary to adopt a better MO method to predict the transition energies of free radicals.

Experimental Section

Materials. Solvents used for the transient absorption measurements were of spectroscopic grade. Commercially available dithio-2,2′-dipyridine (**4**), 2-mercaptopyridine (**5**), dithio-2,2′-dibenzothiazole (**7**) , and dienes were used. Disulfide **8** was prepared by the photolysis of a 1:1 mixture of **4** (0.02 M) and **7** (0.02 M) in N_2 bubbled benzene solution with the steady-light longer than 270 nm of Xe−Hg lamp for 1 h . Disulfide **8** was obtained as an almost equimolar mixture with **4** and **7**, which were separated by TLC (Merk; Kiesegel 60F and benzene as an eluent). **8**: 28% yield (expected yield = 33%), solid mp 130 °C (prism from ethanol); UV; λ_{max} = 274 and 223 nm; ^{1}H NMR (CD_3Cl) δ 7.20 (s, 1, ring H), δ 7.39 (m, 3, ring's H), δ 7.80 (m, 3, ring's H), δ 8.50 (s, 1, ring H); HRMS calcd for $C_{12}H_8N_2S_3$, 275.9849, found 275.9849. Anal. Calcd for $C_{12}H_8N_2S_3$: C, 52.17; H, 2.90; N, 10.14. Found: C, 52.39; H, 2.75; N, 9.94.

Apparatus. Laser flash photolysis apparatus was a standard design with Nd:YAG laser of 6 ns duration.[19] Solution was photolyzed with FHG light (266 nm). The time profiles were followed by a photomultiplier system in the visible region. Transient spectra were recorded with a multichannel photodiode system. The laser photolysis was performed for the solution in a rectangular quartz cell with a 10 mm optical path. The monitoring light was selected with the band-path filters. All the measurements were carried out at 23 °C.

MO Calculation. The MO calculations were performed with MNDO method using MOPAC '93 presented by Japan Program Exchange Association.[20]

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