Runs at 60.0° with no **8** showed that Banfield's radical was stable under the kinetic conditions.

Method II. Bis(pyrrolidyl-1) disulfide and Banfield's radical, in the molar ratio of 100:1, were dissolved in 7 ml of reagent grade toluene. This solution was placed in a container with a septum covering one opening and a stopcock closing a second opening. The solution was frozen and degassed as above by pulling a vacuum through the open stopcock. A positive nitrogen pressure was left in the system when the degassing was complete. The whole container was wrapped in aluminum foil and placed in an oil bath as above. Samples were removed with a syringe through the septum, frozen in liquid nitrogen, and analyzed as above.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXII. Dialkylaminothiyl Radicals[1]

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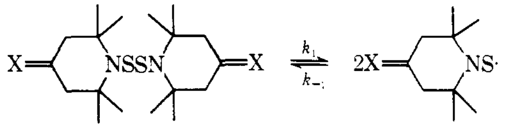
Abstract: The equilibria between 2,2,6,6-tetramethylpiperidyl-1-thiyl and diisopropylaminothiyl and the corresponding bis(dialkylamino) disulfides have been examined by EPR spectroscopy: $R_2NSSNR_2 \rightleftharpoons 2R_2NS$ (k_1, k_{-1}). Within experimental error, the equilibrium constants are the same for both radicals ($\Delta S = 23 \pm 4$ gibbs/mol, $\Delta H = 27 \pm 2$ kcal/mol), as are the rate constants for disulfide decomposition and radical combination which can be represented, respectively, by $\log (k_1/\text{sec}^{-1}) = 16.8 - 31/\theta$ and $\log (k_{-1}/M^{-1}\ \text{sec}^{-1}) = 11.8 - 4.0/\theta$, where $\theta = 2.3RT$ kcal/mol. These radicals were generated in solution both thermally and photochemically, but photolysis in solid matrices at low temperatures gives some N–S bond scission. Dialkylaminothiyl radicals are unreactive toward a variety of molecular substrates. The first sulfur analogue of an iminoxy radical, diphenyliminothiyl, has been generated by photolysis of the corresponding disulfide. Its EPR parameters are $g = 2.0152$, $a^N = 18.16$ G.

Dialkylaminothiyl radicals, $R_2NS\cdot$, the sulfur analogues of the well-known dialkyl nitroxides, have received no attention since Bennett, Sieper, and Tavs reported on two of these radicals in 1967.[3] These workers detected 2,2,6,6-tetramethylpiperidyl-1-thiyl (**1**) and 2,2,6,6-tetramethyl-4-oxopiperidyl-1-thiyl (**2**) radicals by EPR spectroscopy during the thermolysis of the corresponding disulfides in iodobenzene at temperatures in the range 90 to 200°. The intensity of the EPR signals increased and decreased reversibly as the temperature was raised and lowered, which suggested that the radicals were formed reversibly. The possibility that the equilibrium was an artifact and that the radicals



1, X = H_2
2, X = O

were actually destroyed by a reaction which did not re-form disulfide was not explored.

We have re-examined Bennett, Sieper, and Tavs reaction with **1** and with diisopropylaminothiyl (**3**). These radicals were generated both thermally and photochemically. By measuring the rate constant for radical decay (k_{-1}) by kinetic EPR spectroscopy, we have been able to confirm the existence of a true radical-dimer equilibrium. This has enabled us to measure the S-S bond strength in the dimers and examine some of the properties of aminothiyl radicals.

After completion of this work, we learned of Danen and Newkirk's[4] very similar studies. Our own results tend to complement theirs, and the two studies are in general agreement, though there are differences on some points that will need further examination.

In this paper, we also report the EPR spectral parameters for the diphenyliminothiyl radical, $Ph_2C{=}NS\cdot$, the first sulfur analogue of the well-known iminoxy radicals to be detected. Unfortunately, we were not able to generate any dialkyliminothiyl radicals.

Experimental Section

General Procedure. All EPR samples contained accurately known concentrations of dimer (0.1-1.0 *M*) in research grade solvents that had been freed from polar impurities by passage over basic alumina. The samples were carefully degassed by four or more freeze-thaw cycles. Spectra were obtained on a Varian E-4 EPR spectrometer. The radicals were generated both by thermolysis and by photolysis directly in the cavity of the spectrometer. The measurement of radical concentrations and the kinetic EPR technique have been adequately described in earlier publications.[5]

Materials. Bis[2,2,6,6-tetramethylpiperidyl-1] disulfide (dimer of **1**) was prepared by the action of S_2Cl_2 on 2,2,6,6-tetramethylpiperidine as described by Bennett *et al.*,[3] mp 86-86.5° (lit.[3] 84-85°). Anal. Calcd for $C_{18}H_{36}N_2S_2$: C, 62.73; H, 10.53; N, 8.13. Found: C, 62.66; H, 10.51; N, 8.20.

Bis[diisopropylamino] disulfide (dimer of **3**) was prepared by the method of Michaelis and Luxembourg[6] by reaction of diisopropylamine with S_2Cl_2: yellow liquid, purified by distillation under high vacuum, n^{21}D 1.5049. Anal. Calcd for $C_{12}H_{28}N_2S_2$: C, 54.49; H, 10.67; N, 10.59. Found: C, 54.66; H, 10.70; N, 10.41.

Bis[diethylamino] disulfide was prepared by the same procedure and purified by distillation under high vacuum: yellowish liquid, n^{21}D 1.5122. Anal. Calcd for $C_8H_{20}N_2S_2$: C, 46.11; H, 9.62; N, 13.44. Found: C, 46.29; H, 9.49; N, 13.51.

Bis[piperidyl-1] disulfide was prepared by the same procedure and purified by recrystallization from ethanol, mp 65-66° (lit.[6] 64°). Anal. Calcd for $C_{10}H_{20}N_2S_2$: C, 51.68; H, 8.67; N, 12.05. Found: C, 51.23; H, 8.65; N, 11.68.

Bis[diphenylimino] disulfide (dimer of **5**) was prepared by the method of Exner[7] from phenylmagnesium bromide, benzonitrile, and sulfur monochloride and was recrystallized from 3:1 benzene-ethanol, mp 176-176.5° (lit.[7] 176°). Anal. Calcd for $C_{26}H_{20}N_2S_2$: C, 73.55; H, 4.74; N, 6.60. Found: C, 73.62; H, 4.50; N, 6.42.

The same general procedure was used in (apparently unsuccessful) attempts to prepare bis(diisopropylimino) disulfide and bis(di-*tert*-butylimino) disulfide. The raw products were fractionated by distillation under high vacuum. However, none of the fractions gave, upon photolysis, EPR spectra that could be attributed to dialkyliminothiyl radicals and, therefore, further work along these lines was abandoned.

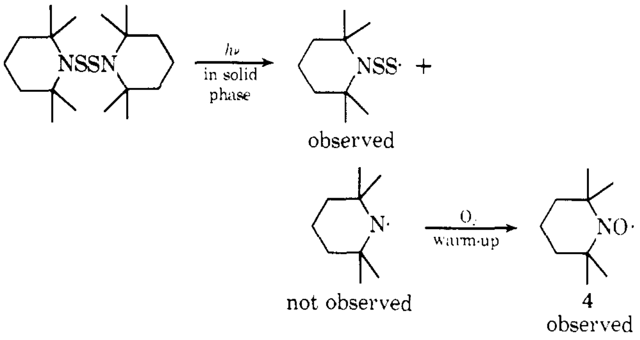
Results

EPR Spectra. For best resolution, EPR spectra of dialkylaminothiyl radicals were recorded during photolysis of hydrocarbon solutions of the disulfides at temperatures somewhat below ambient. Under these conditions, the nitrogen coupling is readily resolved with 2,2,6,6-tetramethylpiperidylthiyl (**1**) and with diisopropylaminothiyl (**3**), the methine hydrogens also being partially resolved in the latter case: **1** at 0°, a^N = 11.41 G, g = 2.0178 (lit.[3] a^N = 11.4, g = 2.0173); **3** at −40°, a^N = 10.9 G, $a^H(2H)$ = 2.4 G, g = 2.0159. However, we were never able to resolve the nitrogen couplings with diethylaminothiyl and piperidylthiyl probably because of unresolved proton splittings. In each case, a single broad line was obtained having a g value in the range expected for aminothiyls, viz., 2.017 ± 0.001.

Table I. Rate Constants for Decay of 2,2,6,6-Tetramethylpiperidyl-1-thiyl (**1**) and Diisopropylaminothiyl (**3**) in *tert*-Butylbenzene

Radical (range in concn, *M*)	Temp, °K	$k_{-1} \times 10^{-8}$ M^{-1} sec^{-1}
1 (3-15 × 10^{-7})	229	1.0
	247	1.7
	267	3.5
	286	8.2
	298	8.3
3 (3-9 × 10^{-7})	225	1.0
	248	2.3
	262	3.4
	284	6.0

EPR signals due to other radicals were sometimes obtained during photolysis and thermolysis of the disulfides. For example, **1** was often accompanied by a 2-G doublet, $g \sim 2.005$, which could be saturated at high power levels. While no attempt was made to identify and study these "impurity" radicals, we did observe that photolysis of *frozen* hydrocarbon solutions of all the disulfides gave an anisotropic EPR signal with principal g values of 2.003, 2.033, and 2.051. This signal is characteristic of RSS· radicals in matrices.[8] It suggests that photolysis in the solid state can cleave the N-S bond. This was confirmed by photolysis of an oxygen saturated frozen solution of bis[tetramethylpiperidyl-1] disulfide. The normal anisotropic signal appeared in the solid, but on turning off the light and warming the sample until it melted, this signal was replaced by the spectrum of 2,2,6,6-tetramethylpiperidyl-*N*-oxyl (**4**). When this disulfide was photolyzed in oxygen saturated solutions, only **1** is detected. Since **4** is a very persistent radical, it would seem that N-S cleavage is, for some reason, confined to photolysis in matrices.



Kinetics of Radical Decay. Both 2,2,6,6-tetramethylpiperidylthiyl and diisopropylaminothiyl were generated by photolysis of their disulfides in *tert*-butylbenzene in the EPR cavity, and their decay was monitored by kinetic EPR spectroscopy. The radicals both decay extremely rapidly with very "clean" second-order kinetics[9] and at approximately equal rates (see Table I). These decay reactions are almost certainly diffusion controlled, the increase in the measured rate constant with increasing temperature being due to the decreasing viscosity of the solvent rather than to

Table II. Some Typical Experimental Data for the Radical 1–Dimer Equilibrium in *tert*-Butylbenzene

Temp, °K	Dimer concentration at 23°: 0.110 M			0.577 M
	$[1] \times 10^6, M$	$K \times 10^{12}, M$	$[1] \times 10^6, M$	$K \times 10^{12}, M$
404	9.1	830		
390	4.4	189	8.9	150
374	2.1	43	4.3	35
360	0.82	6.5	1.8	5.8
344	0.47	2.1	0.76	1.0
328			0.34	0.21
313			0.13	0.03

Table III. Van't Hoff Parameters for Dialkylaminothiyl Radical–Dimer Equilibria

Radical	Solvent	ΔS, gibbs/mol	ΔH, kcal/mol
1	*tert*-Butylbenzene	27 ± 7	28 ± 2.5
1	Iodobenzene	20 ± 4	26 ± 2
3	*tert*-Butylbenzene	16 ± 8	24 ± 3

any intrinsic activation energy for the decay process. The rate constant for decay of either radical can be represented by

$$\log (k_{-1}/M^{-1}\ \text{sec}^{-1}) = 11.8 - 4.0/\theta$$

where $\theta = 2.3RT$ kcal/mol.[10]

Radical–Dimer Equilibrium. Radicals **1** and **3** can both be readily detected if solutions of their disulfides are warmed to temperatures in the range 40–130°, and in this range the radical concentration can be increased and decreased reversibly by raising and lowering the temperature. That this phenomenon is, in fact, due to the occurrence of the equilibrium

$$R_2NSSNR_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2R_2NS\cdot$$

is indicated by the high steady-state concentration of radicals that is obtained and can be maintained for prolonged periods at the higher temperatures. The high rate constant for the bimolecular self-reactions of dialkylaminothiyl radicals would require that the "steady-state" radical concentration decrease rather quickly if any significant fraction of the radicals decayed by a route other than dimerization. At still higher temperatures the radicals do decay by other routes.[3]

We have determined the equilibrium constants, $K_1 = (k_1/k_{-1})$ (corrected for thermal expansion of the solvent), for the equilibrium of **1** and **3** with their disulfides by measuring the concentrations of the radicals produced by warming solutions of the disulfides. Typical data for **1** in *tert*-butylbenzene are given in Table II. The equilibrium constants measured over a range of temperatures can be represented by the van't Hoff relation, $K_1 = e^{\Delta S/R}e^{-\Delta H/RT}$. Values of ΔH and ΔS are summarized in Table III. Considering the experimental errors, it would appear that ΔH and ΔS do not depend on the solvent (*tert*-butylbenzene or iodobenzene) or on the nature of the alkyl groups (**1** and **3**). Combining all our data gives as the "best" values for ΔS and ΔH, 23 ± 4 gibbs/mol and 27 ± 2 kcal/mol, respectively. The S–S bond dissociation energy of the two disulfides is, of course, equal to ΔH.

Combination of these van't Hoff parameters with the Arrhenius parameters for k_{-1} gives, for the disulfides yielding **1** or **3**,

$$\log (k_1/\text{sec}^{-1}) = 16.8 - 31/\theta$$

This result may be compared with that obtained by Danen and Newkirk[4] who measured the rate of decomposition of *N,N'*-dithiobispyrolidine by trapping the aminothiyl radicals with Banfield's radical and obtained $\log (k_1/\text{sec}^{-1}) = 14.68 - 31.5/\theta$. The activation energies for S–S cleavage are in excellent agreement, but our preexponential factor is closer to that "normally" found for a unimolecular bond scission.[12]

Passivity of Dialkylaminothiyl Radicals. A few unsuccessful attempts were made to react **1** and **3** with molecular substrates that are usually quite reactive to the majority of free radicals. For example, photolysis of solutions of either disulfide in the presence of oxygen, 1-decene, 1,1'-di-*tert*-butylethylene,[13] triethyl phosphite, and triethylphosphine yielded EPR spectra only of the appropriate dialkylaminothiyl radical. Therefore these radicals are inert to oxygen, do not add readily to olefins, are not desulfurized by phosphites,[14] and do not undergo homolytic substitutions at the phosphorus of trialkylphosphines.[15] Photolysis of either disulfide in the presence of 2,4,6-tri-*tert*-butylphenol gave aminothiyl and tri-*tert*-butylphenoxy radicals. However, these two radicals were formed in about the same concentrations in two blank experiments using the individual substrates, and so they must be produced independently. That is, aminothiyl radicals do not abstract hydrogen even from such good donors as hindered phenols.

Diphenyliminothiyl (5). Photolysis of a saturated solution of bis(diphenylimino) disulfide in *tert*-butylbenzene gives an EPR spectrum which shows that three radicals (**5**, **6**, and **7**) are formed. None of these radicals are saturated by high levels of microwave power (50 mW). The spectrum of radical **5** consists of a 1:1:1 triplet, $g = 2.0152$, $a^N = 18.16 \pm 0.09$ G, and we assign these lines to the desired diphenyliminothiyl radical.

$$Ph_2C{=}NSSN{=}CPh_2 \xrightarrow{h\nu} 2Ph_2C{=}NS\cdot$$

5

Radical **6** shows only a single line, $g = 2.0214$, which is of lower intensity than the lines due to **5**. Perhaps this radical is $Ph_2C{=}NSS\cdot$, but photolysis in the presence of oxygen did not yield the expected iminoxy radical, $Ph_2C{=}NO\cdot$. Radical **7** gave a strong 1:2:1 triplet, $g = 2.0042$, $a^H(2H) = 1.5$ G. This radical is extremely persistent ($\tau_{1/2}$ of days at room temperature) which explains the strong EPR signal from a radical that is probably formed from a decomposition product of the disulfide rather than via direct photolysis of the disulfide. Radical **7**, but not radical **5**, can also be formed by heating solutions of the disulfide to ca. 160°. The structure of **7** remains a mystery.

Radical **5** decayed instantly when the light was cut off. No attempt was made to determine the kinetics and rate constant for this decay in view of fact that radicals **6** and **7** were always present when **5** was generated.

Attempts to prepare bis(dialkylimino) disulfides were unsuccessful (see Experimental Section), and so we were not able to prepare a dialkyliminothiyl radical.

Discussion

As Bennett et al.[3] have pointed out, the EPR spectra of $R_2NS\cdot$ and $R_2NO\cdot$ radicals are basically similar because their main feature is a 1:1:1 triplet caused by interaction of the unpaired electron with the ^{14}N nucleus. The higher g factor for the aminothiyl radicals (~2.017 vs. ~2.006 for nitroxides) is a consequence of the larger spin-orbit coupling constant for sulfur than for oxygen. The smaller nitrogen hyperfine splitting in aminothiyls (~11 G vs. ~15 G in nitroxides) is a consequence of the lower electronegativity of sulfur which makes the dipolar structure $R_2N\cdot^{+}{-}X^{-}$ more disfavored, relative to the $R_2N{-}X\cdot$ structure, for $R_2NS\cdot$ than for $R_2N\dot{O}$. The same factors dominate the EPR spectrum we have assigned to diphenyliminothiyl, $Ph_2C{=}N\dot{S}$. That is, the g factor for this radical is much larger than that found for iminoxy radicals (i.e., 2.015 vs. ~2.005) while the nitrogen splitting is smaller (i.e., 18 vs. ~32 G).

From a chemical point of view, $R_2NS\cdot$ radicals are virtually unique. They couple at (or near) the diffusion-controlled limit but are extremely unreactive toward many molecular substrates that react readily with a majority of free radicals. In this latter aspect, their behavior is analogous to that of nitroxides. However, in their ready head-to-head dimerization, the behavior of aminothiyl radicals differs from nitroxides since only relatively unhindered nitroxides couple reversibly,[5,16,17] and this coupling probably involves a four-center dipole–dipole bond rather than an O to O coupling. The bond strengths in the nitroxide dimers ($\Delta H \leq 8$ kcal/mol)[17] are less than one-third as large as the bond strengths in the aminothiyl radical dimers (ca. 27 kcal/mol). These differences can be attributed to the greater strength of S–S bonds compared with O–O bonds. Our failure to cleave the S–S bond of bis(diphenyliminyl) disulfide by heating can also be accounted for on bond strength grounds since, in the case of the oxygen analogues, it is known that iminoxy radicals form stronger O–R′ bonds than do nitroxides.[18]

Our results confirm Bennett et al.'s conclusion that bis(dialkylamino) disulfides can be reversibly decomposed by heating to yield dialkylaminothiyl radicals. The S–S bond strength is ca. 27 kcal/mol, and this bond can be cleaved by uv photolysis in solution. However, in solid matrices, photolysis leads to at least some N–S bond cleavage.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXIII. Cyanomethyl Radicals[1]

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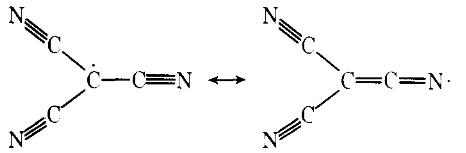
Abstract: Dicyanomethyl and tricyanomethyl have been prepared and examined by EPR spectroscopy. Their EPR parameters at 20° are: $H\dot{C}(CN)_2$, $g = 2.0033$, $a^{H} = 19.18$, $a^{N} = 2.75$, $a^{^{13}C_\alpha} = 29.18$ G; $\dot{C}(CN)_3$, $g = 2.0033$, $a^{N} = 2.28$, $a^{^{13}C_\alpha} = 22.06$, $a^{^{13}C_\beta} = 18.20$. It is concluded, on the basis of the $^{13}C_\alpha$ couplings and from the results of INDO calculations, that both radicals are planar. The $^{13}C_\alpha$ couplings, which were measured with enriched material, increase slightly with increasing temperature because the magnitude of the out-of-plane vibrations of the C_α substituents increases. Both radicals decay with second-order kinetics, the $H\dot{C}(CN)_2$ radical at close to the diffusion-controlled limit ($k^2{}_{EPR} = 1.2 \times 10^9\ M^{-1}\ sec^{-1}$ at 20°), but $\dot{C}(CN)_3$ decays considerably more slowly.

It has been conclusively demonstrated that the majority of long-lived carbon-centered radicals owe their persistence *primarily* to steric effects.[3] Radicals of the triphenylmethyl type are probably no exception,[3] but with such radicals it is difficult to separate the steric influence of the three aromatic rings from the effect they have by virtue of their ability to delocalize the unpaired electron. For this reason, we decided to investigate the kinetic behavior of a carbon radical which, though similar to triphenylmethyl in having three adjacent π-bond systems capable of delocalizing the unpaired electron, had only minimal steric protection of the radical center. As our radical we chose tricyanomethyl, $\dot{C}(CN)_3$, which should be long-lived *if* p-π delocalization



does indeed contribute significantly to persistence. Because of this delocalization, tricyanomethyl is expected to be planar. However, with three highly electronegative groups it was not utterly inconceivable that $\dot{C}(CN)_3$ would be nonplanar (like $\dot{C}F_3$[4] and $\dot{C}Cl_3$[5]). This makes its EPR spectroscopy particularly interesting.

Tricyanomethyl has not been reported, but there have