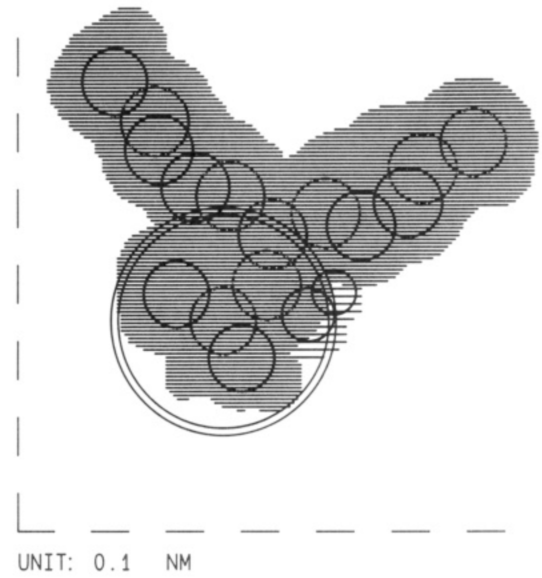

Figure 4. Cut through the van der Waals body of 1,1-dimesityl-3,3-dimethyl-1-buten-2-ol, **1e**.

least hindered α-H enol **1a** (Figure 3) and of the most hindered α-t-Bu enol **1e** (Figure 4). Hatching represents the section through the molecular body; sparse hatching pinpoints the hydroxyl group (up, right in Figure 3; bottom, right in Figure 4). In addition, circles indicate the position of carbons within 0.4 Å of the plane of cut. Hydrogens (apart from the hydroxylic) and other carbons are not marked. The plane of cut is parallel to the first inertial plane of the molecule, and passes through an assigned anchor atom. The external circle is the anchor sphere and to aid in visualization, the figures include an internal sphere, of radius r equal to the volume of a sphere of volume V^a (i.e. $r = 3V^a/4\pi)^{1/3}$). The more encumbered is the anchor, the narrower becomes the intercircle ring.

Notable features in Figures 3 and 4 are that the mesityl groups are locked into positions that are very far from coplanar and that the substituent affects the spatial relationship of the mesityls. In **1a** (Figure 3) the rings are at an appreciable angle whereas for **1e** (Figure 4) they are nearly parallel. In both cuts, the substituent head serves as anchor. In Figure 3, the anchor is H, V^a is quite small, 58.2 Å^3, and the ring between the circles is relatively wide. In Figure 4, the anchor is the tertiary carbon, the ring is thin, and V^a is enormous, 92.7 Å^3. This constitutes 82% of the conceivable maximum of 113.1 Å^3 for a sphere with a radius of 3 Å.

Acknowledgment. This work was partly supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which we are grateful.

N^1,N^5-Bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienyl Radicals. An Electron Spin Resonance Study[1]

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A new class of nitrogen-centered free radicals, N^1,N^5-bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienyl radicals **1** have been generated by hydrogen atom abstraction from N^1,N^5-bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienes **2** or by photolysis of **2** or N^1,N^5,N^5-tris(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienes **3** using a UV or xenon lamp. Radicals **1** persist in solution and can be isolated as a diamagnetic dimer which, in solution, dissociates in part into **1** at room temperature. The thermodynamic parameters for the $\mathbf{4} \rightleftharpoons 2(\mathbf{1})$ equilibrium are 87.5 kJ mol^{-1} (ΔH°) and 153 J K^{-1} mol^{-1} (ΔS°), respectively. Radicals **1** have afforded the ESR spectra that show a_{N^1} (and a_{N^5}) 0.400–0.431, a_{N^3} 0.278–0.312, $a_{^{33}S}$ 0.48, and a_H (due to the protons of the arylthiyl groups) 0.022–0.076 mT. On the basis of these ESR results, it is concluded that in **1** the unpaired electron resides mainly on the three nitrogen and two sulfur atoms.

Recent interest in the chemistry of free radicals has been stimulated by the suggestion that polyradicals might be possible organic ferromagnets.[2] For the realization of such materials, the electron spins in the toporegulated π-networks of polyradicals should be appropriately arranged so as to induce ferromagnetic interactions among the spins. However, advances in this field have been seriously limited by the difficulties in the syntheses of such polyradicals because free radicals suitable for the syntheses of such polyradicals are rare.[3]

For the past 10 years, we have studied thioaminyl radicals ($R\dot{N}SR'$) and their analogues by ESR spectroscopy. In previous papers, we reported that some thioaminyls persist in solution for a long period, even in the presence of the atmospheric oxygen, and can be isolated as pure radical crystals[4,5] or diamagnetic dimers having a very low N–N bond strength.[6,7] As part of a program directed

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(1) ESR Studies of Nitrogen-Centered Free Radicals. 39. Part 38: Miura, Y.; Shibata, Y. *Chem. Express* **1990**, *5*, 573.

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(3) (a) Forrester, A. R.; Hay, J. M.; Thomson, R. H. In *Organic Chemistry of Stable Free Radicals*; Academic Press: New York, 1968. (b) Rozantsef, E. G. In *Free Nitroxide Radicals*; Plenum Press: New York, 1970 (translated from Russian by Hazzard, B. J.). (c) Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 455.

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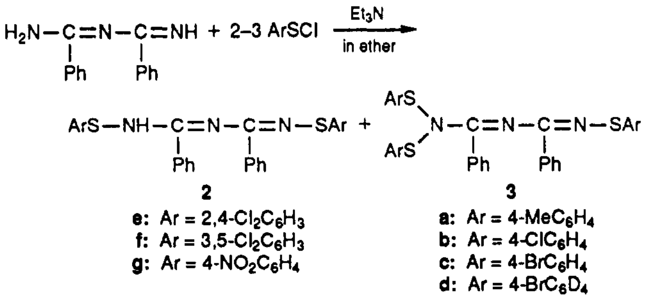
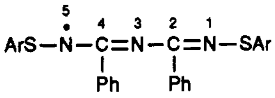
(6) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875.

Scheme I



toward the syntheses of high-spin or ferromagnetic materials, we have searched thioaminyls having the structures suitable for the syntheses of ferromagnetic materials. In this paper, we describe the generation, ESR spectra, and stabilities of N^1,N^5-bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienyl radicals (1).



$$\mathrm{ArS{-}\overset{5}{\overset{\bullet}{N}}{-}\underset{Ph}{\overset{4}{C}}{=}\overset{3}{N}{-}\underset{Ph}{\overset{2}{C}}{=}\overset{1}{N}{-}SAr}$$

1

Results and Discussion

Generation of Radicals 1. Precursors 2 and 3 were obtained by the reaction of 2,4-diphenyl-1,3,5-triazapenta-1,3-diene with 2–3 equiv of arenesulfenyl chlorides. The diene is readily obtained as the corresponding hydrochloride hemihydrate by the reaction of N-benzoylbenzamidine with benzamidine, followed by treatment with HCl.[8] After neutralization of the diene hydrochloride with K_2CO_3, the free diene was allowed to react with arenesulfenyl chlorides in the presence of triethylamine. When arenesulfenyl chlorides having an electron-withdrawing substituent were employed in this reaction, the reaction mixtures afforded 2 in 15–59% yield after column chromatographic separation. On the other hand, when arenesulfenyl chlorides having an electron-donating substituent were employed, the reaction mixtures gave 3 in 60–79% yields (Scheme I).

For the ESR measurements, radicals 1 were generated by three methods: (1) photolysis of 2 or 3 with a high-pressure mercury lamp or a xenon lamp; (2) the reaction of 2 with di-*tert*-butyl diperoxyoxalate (DBPO); (3) oxidation of 2 with PbO_2. Radicals 1 persisted in solution, even in the presence of oxygen. This was shown by a brief kinetic study; that is, although the ESR spectra from a benzene solution of 1 in an open ESR cell were followed for 6 h at room temperature in the dark, no or negligibly small decay in the ESR spectra was found.

The ESR spectra of 1 were considerably complex, as found in Figure 1. If the three nitrogen atoms (N^1, N^3, and N^5) are magnetically equivalent, the spectra should be split into a septet with the intensity ratio of 1:3:6:7:6:3:1. However, the ESR spectra obtained did not show such an intensity ratio; the ratio was more complex; this indicates that N^1 and N^5 are magnetically inequivalent to N^3. To confirm this, the aromatic protons of the two arylthiyl groups were replaced with deuteriums, since the corresponding ESR spectrum was expected to be simplified by removal of the splittings from the aromatic protons of the arylthiyl groups. As expected, the deuterated radical 1d gave a simpler ESR spectrum consisting of a 1:2:3:2:1 quintet of 1:1:1 triplets, as found in Figure 2. From this spectrum, a_{N^1} (and a_{N^5}) and a_{N^3} were determined to be 0.404 and 0.278 mT for 1d, respectively.

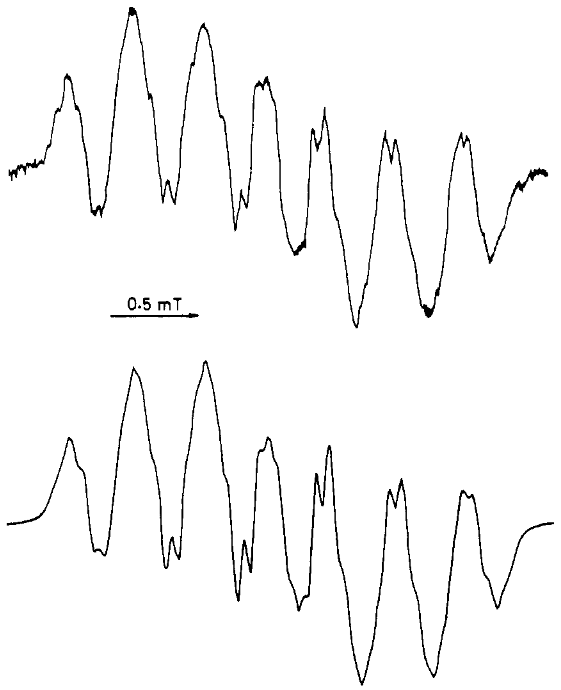


Figure 1. Experimental ESR spectrum (top) of 1a generated by photolysis of a benzene solution of 3a with a 100-W high-pressure mercury lamp and a computer-simulated ESR spectrum (bottom) reconstructed by using the ESR parameters listed in Table I.

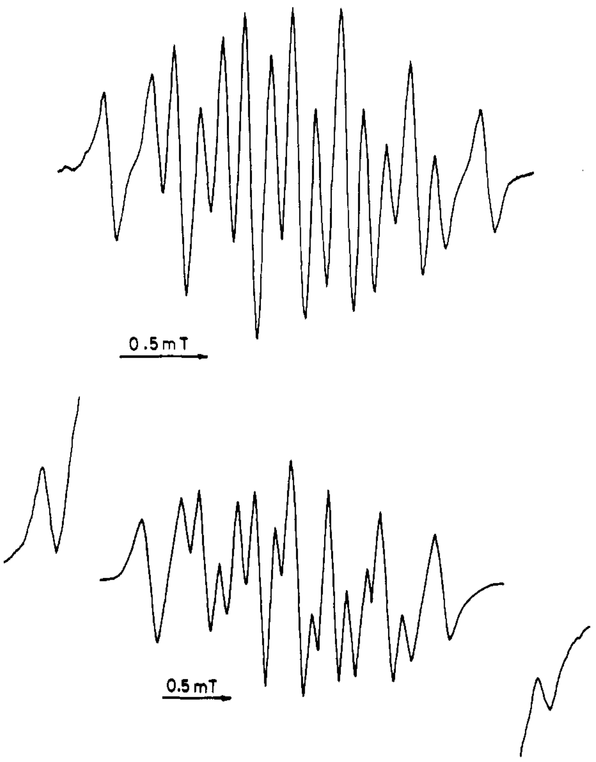


Figure 2. Experimental ESR spectra of 1d generated by photolysis of a benzene solution of 3d. The top spectrum was obtained from a low-concentration solution of 1d, while the bottom spectrum was obtained from a high-concentration solution of 1d. In the bottom spectrum, both wings are recorded at high gain (200 times), and satellite lines ($M_N = +1$, $M_S = +^3/_2$ and $M_N = -1$, $M_S = -^3/_2$) due to ^{33}S isotopes at natural abundance are found.

Since radicals 1 bear two sulfur atoms in the π-framework accommodating the unpaired electron, it seemed to

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Table I. ESR Parameters for 1 in Benzene at 296 K[a]

radical	$a_{N\text{-}3}$	$a_{N\text{-}1,5}$	$a_{o\text{-}H}$[b,c]	$a_{m\text{-}H}$[b,c]	$a_{p\text{-}H}$[b,c]	a_{other}	g
1a	0.279	0.400	0.074 (4)	0.024 (4)		0.089 (2CH$_3$)	2.0075
1b	0.286	0.410	0.073 (4)	0.022 (4)		0.48 (2^{33}S)	2.0075
1c	0.280	0.407	0.072 (4)	0.023 (4)			2.0081
1d	0.278	0.406				0.48 (2^{33}S)	2.0081
1e	0.290	0.417	0.067 (2)	0.023 (4)			2.0076
1f	0.296	0.431	0.076 (4)		0.064 (2)		2.0071
1g	0.312	0.417					2.0074

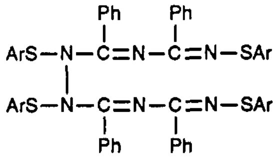
[a] Hyperfine splitting constants are given in mT and determined by computer simulation. [b] Due to the protons of the arylthiyl groups. [c] The numbers in parentheses refer to the number of equivalent protons.

be important to evaluate the magnitudes of $a_{^{33}S}$ for the elucidation of the spin density distribution in 1. However, satellite lines due to ^{33}S isotopes at natural abundance (0.76%) are generally very difficult because the intensity of the satellite lines due to ^{33}S isotopes are only 0.19% of the parent spectrum. Fortunately, when a high-power xenon lamp (1 kW) was used as a source for photolysis and the spectrum was recorded at high gain, we could detect two satellite lines ($M_N = +1, M_S = +^3/_2$ and $M_N = -1, M_S = -^3/_2$) from ^{33}S isotopes at natural abundance in the wings of the parent spectrum, as found in Figure 2. Assignment of the ^{33}S satellite lines was performed by the intensity ratio of the satellite lines to the parent spectrum (experimental, 0.39%; theoretical, 0.38% for two sulfur atoms). For **1b**, two satellite lines from ^{33}S isotopes at natural abundance were also observed, although these are significantly masked by the parent spectrum. The hyperfine splitting (hfs) constants and g values for 1 are summarized in Table I.

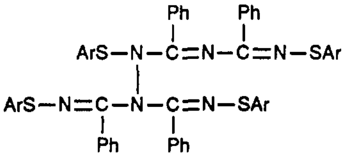
Isolation and Characterization of Dimer 4e. Radicals 1 were found to be in equilibrium with a diamagnetic dimer 4. When a radical solution of 1 was raised to a high temperature, the ESR spectrum was enhanced, when the radical solution was cooled to a low temperature, the ESR spectrum was weakened, and this cycle was completely reversible. This finding prompted us to isolate the dimer, and **4e** was isolated in 75% yield as light yellow prisms by the following procedure: a solution of **2e** in benzene was treated with PbO$_2$ in the presence of K$_2$CO$_3$. After filtration, the solvent was removed by freeze drying, and the resulting light yellow crystalline powder was crystallized from hexane.

The structure was confirmed by IR and ^{1}H NMR spectra, elemental analysis, and finally by a single-crystal X-ray analysis. In both IR and ^{1}H NMR spectra, no absorption due to ν NH was found. The IR and ^{1}H NMR spectra also exhibited that the dimer was isolated as the hexane solvate; in the IR spectrum strong absorptions due to ν CH were found at ~2950 cm^{-1}, and in the ^{1}H NMR spectrum triplet (δ 0.88) and singlet peaks (δ 1.27) due to hexane were found. The ratio of hexane to the dimer was determined to be 1.0 from the integrated ^{1}H NMR spectrum. This ratio was further confirmed by the elemental analysis of the dimer. Although the crystals were heated to 90 °C for 3 h, no or negligibly small changes in the IR and ^{1}H NMR spectra were observed, indicating that the hexane molecules tightly bind. Crystallization of **4e** from pentane, 2-octane, cyclohexane, and ethyl acetate also gave solvated crystals.

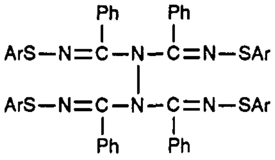
There are three possibilities for the dimer structure, namely, **4e**, **4e′**, and **4e″**. The IR and ^{1}H NMR spectra were, however, helpless for the determination of the correct structure of the dimer. We therefore performed a single-crystal X-ray analysis for the dimer.[9] Recrystallization from ethyl acetate provided crystals of relatively good quality, and the X-ray results exhibited **4e** as the dimer structure, which indicates that the dimerization reaction takes place at N^5 (or N^1).



4e



4e′



4e″

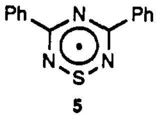
Ar: 2,4-Cl$_2$C$_6$H$_3$

Although dimer **4e** in the solid is diamagnetic, it dissociates, in solution, in part into **1e** readily at room temperature (23 °C). By double integration of the ESR spectra of **1e** from a solution of **4e**, the equilibrium constants (K) for the **4e** ⇄ 2(**1e**) equilibrium were derived in the temperature range 281–306 K, and from a plot of ln K vs $1/T$ the enthalpy of dissociation ($\Delta H°$) and entropy of dissociation ($\Delta S°$) were derived to be 87.5 k J mol^{-1} and 153 J K^{-1} mol^{-1}, respectively, using the eq 2, where R is the gas constant and T is the absolute temperature. The values of K at various temperatures are summarized in Table III.

$$K = \frac{[\text{radical}]^2}{[\text{dimer}]} \tag{1}$$

$$\ln K = -\frac{\Delta H°}{R}\frac{1}{T} + \frac{\Delta S°}{R} \tag{2}$$

ESR Parameters. As can be seen from Table I, radicals 1 give relatively large a_N (0.278–0.431 mT) and $a_{^{33}S}$ values (0.48 mT), indicating that in 1 the unpaired electron resides mainly on the three nitrogen and two sulfur atoms. The high g values (2.0071–2.0081) observed for 1 can therefore be accounted for in terms of the high spin densities on sulfurs having a large spin–orbit coupling parameter (382 cm^{-1}), which shifts the g values to a higher one. We also note that N^1 and N^5 are magnetically equivalent to each other, but these are inequivalent to N^3, and the a_N values for N^1 and N^5 are 1.4 times larger than that for N^3. In the cyclic analogue **5**,[10] the three nitrogen atoms are magnetically equivalent (a_N: 0.397 mT) and their a_N value (0.397 mT) lies between a_{N^1} (or a_{N^5}) and a_{N^3} for 1.



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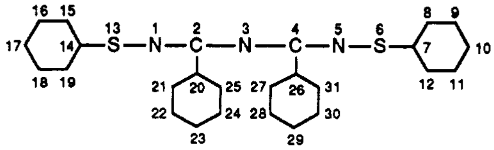
[9] Unpublished results.

[10] Hayes, P. J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346.

Table II. Experimental and Calculated Spin Density Distribution in 1



position	observed hfs const[a] (mT)	exptl spin density[b]	calcd spin density HMO	calcd spin density McLachlan[c]
1,5	0.410	0.186	0.187	0.240
2,4			0.007	−0.032
3	0.286	0.130	0.169	0.219
6,13	0.48	0.21	0.155	0.158
7,14			0.001	−0.009
8,12,15,19	0.073	0.027	0.020	0.019
9,11,16,18	0.022	0.008	0.000	−0.006
10,17			0.020	0.018
20,26			0.000	0.002
21,25,27,31			0.002	−0.005
22,24,28,30			0.000	0.000
23,29			0.002	−0.004

[a] Hyperfine splitting (hfs) constants for **1b**. [b] Calculated from the equation $a_x = Q_x\rho_x^*$, where $Q_H = -2.7$, $Q_N = 2.2$, $Q_{^{33}S} = 2.3$ mT: Miura, Y.; Asada, H.; Kinoshita, M.; Ohta, K. *J. Phys. Chem.* **1983**, *87*, 3450–3455. [c] $\lambda = 0.7$.

Small delocalization of the unpaired electron onto the *S*-phenyl groups is shown by the small proton hyperfine splitting constants of 0.022–0.076 mT. On the other hand, no or negligibly small delocalization of the unpaired electron onto the phenyl groups attached to C^2 and C^4 is shown by no observation of splittings due to the corresponding aromatic protons.

To confirm this spin density distribution in **1**, the Hückel and McLachlan–Hückel MO calculations were performed assuming the radical to be planar and using the following parameters (which have been employed in the calculations of thioaminyl radicals):[7] $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\beta_{CN} = 1.1\beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, $\lambda = 0.7$. Although some deviations are found on N^3 and S, the MO calculations are in good agreement with the experimental results, as found in Table II. That is, the MO calculations predict high spin densities on the nitrogen and sulfur atoms, small delocalization of the unpaired electron onto the *S*-phenyl groups, no or negligibly small delocalization of the unpaired electron onto the phenyl groups attached to C^2 and C^4, and higher spin densities on N^1 and N^5 than on N^3. On the basis of both the experimental results and the MO calculations, we conclude that the unpaired electron is delocalized over the whole of the radical and that the positions of high spin densities are the three nitrogens and two sulfurs.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24B (60-MHz) or JEOL GX-400 (400-MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane used as internal standard.

4-Methyl-, 4-chloro-, 4-bromo-, 4-nitro-, 2,4-dichloro-, and 3,5-dichlorobenzenesulfenyl and 4-bromobenzenesulfenyl-d_4 chlorides were obtained by passing chlorine through a solution of the corresponding arenethiol or diaryl disulfide in dry CH_2Cl_2 at 0 °C or at room temperature. 4-Methylbenzenesulfenyl chloride was purified by distillation, while the other sulfenyl chlorides were used in the follwoing step without further purification.[7] 2,4-Diphenyl-1,3,5-triazapent-1,3-diene hydrochloride hemihydrate was prepared according to the reported procedure and crystallized from ethanol–acetone; mp 202–203 °C (lit.[8] mp 204–206 °C). Di-*tert*-butyl diperoxyoxalate was obtained by the reported method.[11]

4-Bromobenzenethiol-d_4. This compound was prepared by following the procedures reported for benzenethiol,[12] with some modifications. To a stirred solution of 21.9 g (0.135 mol) of bromobenzene-d_5 in 140 mL of $CHCl_3$ was added at 0 °C 65.8 g (0.565 mol) of chlorosulfonic acid, and the resulting solution was stirred for 1 h at the same temperature and then for 1 h at reflux. After being cooled, the reaction mixture was poured into large amounts of ice–water and the chloroform layer was separated and dried ($CaCl_2$). Filtration and evaporation gave 24.6 g (0.095 mol, 70%) of 4-bromobenzenesulfonyl-d_4 chloride as a colorless solid mass.

A mixture of 24.6 g of 4-bromobenzenesulfonyl-d_4 chloride, 48 g of zinc, and 52 mL of sulfuric acid in 290 mL of water was refluxed for 12 h. The reaction mixture was extracted then with ether (100 mL × 3), the combined ether extract was washed with brine, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on silica gel with 1:1 benzene–hexane. Crystallization from ethanol gave 12.2 g (0.063 mol, 67% based on 4-bromobenzenesulfonyl-d_4 chloride) of 4-bromobenzenethiol-d_4: mp 77–79 °C; ^{1}H NMR ($CDCl_3$) δ 3.43 (s, SH, 1 H); *d*-content (determined by ^{1}H NMR) >95%.

General Procedure for Preparation of N^1,N^5-Bis(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienes 2. In a separatory funnel were placed 0.50 g (1.78 mmol) of 2,4-diphenyl-1,3,5-triazapenta-1,3-diene hydrochloride hemihydrate, 50 mL of 10% K_2CO_3 solution, and 80 mL of ether. The mixture was well shaken, and the organic layer was separated and dried (Na_2SO_4). After filtration, the solvent was evaporated under reduced pressure and the resulting colorless viscous oil was dried under vacuum.

The oil was then dissolved in 150 mL of dry ether, and 0.88 g (8.7 mmol) of triethylamine was added. A solution of 4.45 mmol of arenesulfenyl chloride in 30 mL of dry ether was then added dropwise to the solution at 0 °C with stirring. After addition, the reaction mixture was stirred for 1 h at the same temperature and filtered. The filtrate was evaporated under reduced pressure, and the residue was column chromatographed on alumina (Merck, aluminium oxide 90; column size, 3.5 × 18 cm) using 1:1 benzene–hexane (**2e** and **2f**) or 1:10 ethyl acetate–benzene (**2g**) as eluant, giving pure **2**.

N^1,N^5-Bis[(2,4-dichlorophenyl)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (2e): light yellow needles (from hexane); mp 145–146 °C; yield 0.60 g (1.04 mmol, 59%); IR (KBr) 3350 and 3200 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 6.26 and 6.70 (each s, syn and anti NH, 1 H), 7.17–7.94 (m, aromatic, 16 H). Anal. Calcd for $C_{26}H_{17}Cl_4N_3S_2$: C, 54.08; H, 2.97; N, 7.28. Found: C, 53.96; H, 3.03; N, 7.10.

N^1,N^5-Bis[(3,5-dichlorophenyl)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (2f): light yellow needles (from hexane); mp 145.5–147.5 °C; yield 0.144 g (0.258 mmol, 15%); IR (KBr) 3350 and 3160 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 6.26 and 6.61 (each s, syn and anti NH, 1 H), 7.10–7.61 (m, aromatic, 16 H). Anal. Calcd for $C_{26}H_{17}Cl_4N_3S_2$: C, 54.08; H, 2.97; N, 7.28. Found: C, 53.96; H, 3.03; N, 7.10.

N^1,N^5-Bis[(4-nitrophenyl)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (2g): yellow needles (from benzene–hexane); mp 181–183 °C; yield 0.41 g (0.77 mmol; 43%); IR (KBr) 3290 cm^{-1} (NH); 1H NMR ($CDCl_3$) δ 6.36 and 6.82 (each s, syn and anti NH, 1 H), 7.26–8.24 (m, aromatic, 18 H). Anal. Calcd for $C_{26}H_{19}N_5O_4S_2$: C, 58.96; H, 3.62; N 13.23. Found: C, 59.28; H, 3.58; N, 12.86.

General Procedure for Preparation of N^1,N^5,N^5-Tris(arylthio)-2,4-diphenyl-1,3,5-triazapenta-1,3-dienes 3. 2,4-Diphenyl-1,3,5-triazapenta-1,3-diene hydrochloride hemihydrate (0.50 g, 1.78 mmol) was neutralized as described previously and dissolved in 150 mL of dry ether. After addition of 0.87 g (8.7 mmol) of triethylamine, a solution of 5.88 mmol of arenesulfenyl chloride in 30 mL of dry ether was added dropwise to the solution at 0 °C with stirring. The mixture was stirred for 1 h at the same

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[11] Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

[12] Adams, R.; Marvel, C. S. *Organic Synthesis*; Wiley: New York, 1941; *Coll. Vol. I*, p 504.

Table III. Equilibrium Constants (K), Enthalpy of Dissociation ($\Delta H°$), and Entropy of Dissociation ($\Delta S°$) for the 4e ⇄ 2(1e) Equilibrium in Benzene

run	$10^8 K$, M (temp, K)	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}
1[a]	3.95 (281), 8.77 (287), 18.3 (293), 36.9 (299), 72.3 (305)	86.2	149
2[b]	4.70 (282), 10.9 (288), 23.3 (294), 46.5 (300), 94.8 (306)	88.8	156
average		87.5	153

[a] The initial concentration of 4e, 8.06 M. [b] The initial concentration of 4e, 8.20 M.

temperature and filtered. Evaporation of the solvent under reduced pressure gave a viscous oil, which was crystallized from hexane. On standing at 0 °C, an oil was separated and crystallized gradually. For the analytical samples, recrystallizations were repeated.

N^1,N^5,N^5-Tris[(4-methylphenyl)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (3a): light yellow prisms; mp 109–110 °C; yield 0.685 g (1.16 mmol, 63%); ^{1}H NMR (CDCl$_3$) δ 2.33 (s, Me, 9 H), 6.52–7.73 (m, aromatic, 22 H). Anal. Calcd for $C_{35}H_{31}N_3S_3$: C, 71.27; H, 5.30; N, 7.12. Found: C, 71.15; H, 5.31; N, 7.00.

N^1,N^5,N^5-Tris[(4-chlorophenyl)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (3b): light yellow prisms; mp 124–125 °C; yield 0.66 g (1.01 mmol, 60%); ^{1}H NMR (CDCl$_3$) δ 6.75–7.65 (m, aromatic, 22 H). Anal. Calcd for $C_{32}H_{22}Cl_3N_3S_3$: C, 59.03; H, 3.41; N, 6.45. Found: C, 59.08; H, 3.38; N, 6.42.

N^1,N^5,N^5-Tris[(4-bromophenyl)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (3c): light yellow prisms; mp 121–123 °C; yield 0.996 g (1.27 mmol, 68%); ^{1}H NMR (CDCl$_3$) δ 6.70–7.90 (m, aromatic, 22 H). Anal. Calcd for $C_{32}H_{22}Br_3N_3S_3$: C, 48.99; H, 2.83; N, 5.36. Found: C, 49.07; H, 2.89; N, 5.35.

N^1,N^5,N^5-Tris[(4-bromophenyl-d_4)thio]-2,4-diphenyl-1,3,5-triazapenta-1,3-diene (3d): light yellow prisms; mp 109–112 °C, yield 1.17 g (1.47 mmol, 79%); ^{1}H NMR (CDCl$_3$) δ 7.00-7.50 (m, aromatic, 10 H). Anal. Calcd for $C_{32}H_{10}Br_3D_{12}N_3S_3$: C, 48.25; H, 2.78; N, 5.28. Found: C, 48.19; H, 2.83; N, 5.06.

Isolation of Dimer 4e. To a vigorously stirred mixture of 0.20 g (0.346 mmol) of 2e and 4.0 g of K_2CO_3 in 30 mL of benzene was added 4.0 g of PbO_2 in some portions for 4 min, and the mixture was stirred for an additional 1 min. After filtration, the solvent was removed by freeze drying and the resulting crystalline residue was crystallized from hexane to give 4e in 75% yield (160 mg, 0.129 mmol) as light yellow prisms with mp 118–122 °C. From the ^{1}H NMR spectrum and the elemental analysis, the crystals were found to be a 1:1 complex of 4e and hexane: IR (KBr) 3050, 2950–2850, 1620, 1590, 1580, 1540, 1480, 1440, 1370, 1270, 1140, 1090, 1060, 1030, 950, 860, 800, 760, 750, 720, 700, 640, 580, 540 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, J = 6.8 Hz, Me, 6 H),[13] 1.27 (s, (CH$_2$)$_4$, 8 H),[13] 7.00–8.10 (m, aromatic, 32 H). Anal. Calcd for $C_{52}H_{32}Cl_8N_6S_4 + C_6H_{14}$: C, 56.22; H, 3.74; N, 6.78. Found: C, 55.87, H, 3.71; N, 6.77.

Generation of Radicals 1. For the ESR measurements, samples were prepared by three methods. Method 1: 2 or 3 (20 mg) and benzene (0.40 mL) were placed in an ESR cell. After the solution was degassed by three freeze–pump–thaw cycles using a high-vacuum system, the ESR cell was sealed off and irradiated with a high-pressure mercury lamp (100 W) or a xenon lamp (1 kW) at room temperature. ESR spectra were recorded during the photolysis or after cease of the photolysis. Method 2: 2 (20 mg), DBPO (10 mg), and benzene (0.40 mL) were placed in an ESR cell. After the solution was degassed and the ESR cell was sealed off, the ESR spectra were recorded at room temperature. Method 3: a mixture of 2 (40 mg), K_2CO_3 (0.8 g), and PbO_2 (0.8 g) in benzene (3 mL) was stirred for 4 min at room temperature and filtered. After 0.40 mL of the filtrate was placed in an ESR cell and degassed, the ESR cell was sealed off and the ESR spectra were recorded at room temperature.

ESR Measurements. ESR spectra were recorded on a JEOL JES ME-3X or JEOL JES-FE-2XG spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants and g values were determined by the simultaneous measurement with a dilute Fremy's salt in K_2CO_3 aqueous solution (a_N 1.309 mT; g 2.0057) as reference. Estimated accuracy: ±0.01 mT for hyperfine splitting constants and ±0.0002 for g.

Measurements of Equilibrium Constants. In an ESR cell was placed 0.80 mL of a benzene solution of 4e. After the solution was degassed, the cell was sealed off and set in the cavity of an ESR instrument and double-integrated ESR spectra were recorded. Calibration curves were drawn with 1,3,5-triphenylverdazylbenzene solutions[14] using the same ESR cell and the same instrument settings. Radical concentrations of 1 were determined at five different temperatures between 281 and 306 K for each sample. The results are summarized in Table III.

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[13] These absorptions are attributable to hexane.

[14] Kuhn, R.; Trischmann, H. *Monatsh. Chem.* **1964**, *95*, 457.