shift corresponds to an increase in the size of the cluster from 7.27 Å for Ag_n^{q+} to 7.39 Å for Ag_n^{p+} .

Conclusion

Besides the low nuclearity silver cluster cations Ag_2^+ and Ag_3^{2+} which can be formed in zeolites X and Y,²⁰ we have obtained evidence for a higher nuclearity cluster cation Ag_n^{q+} , the optical spectroscopy of which suggests that n is in the range of 5-13. The thermal and oxidative stabilities of this cluster are consistent with a cationic formulation and location probably on the wall of the α -cage. Under conditions of high silver ion exchange, agglomeration to larger silver clusters occurs apparently at the expense of Ag_n^{q+} . The 220–300-nm induced photochemistry observed for Ag_n^{q+} can be understood in terms of photoionization of a lattice oxygen to produce a V center, with simultaneous reduction of Ag_n^{q+} to Ag_n^{p+} . Support for this idea stems from the observation that the photoredox process $Ag_n^{q+} \rightarrow Ag_n^{p+}$ can be reversed thermally at 500 °C in an Ar atmosphere. By contrast, in a CH₄ atmosphere the photogenerated V center is thought to be chemically quenched, forming a surface hydroxyl group and methyl radicals, the latter dimerizing to gaseous C_2H_6 . Under these circumstances the $Ag_n^{p+} \rightarrow Ag_n^{q+}$ reverse redox process is thermally impeded.

From this and earlier studies it is clear that one must now address the problem of the charge dependence of the electronic and magnetic properties of low nuclearity silver clusters in weakly and strongly interacting supports. In this spirit, we have initiated an SCF-X α -SW MO study of model silver clusters Ag_n^{q+} (where n = 2 to 6 and q =0 to n-1). The results of these calculations will be presented in a later publication.²¹

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Electron Spin Resonance Study of N-Alkyl-N-(alkylthio)aminyl Radicals¹

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A variety of N-alkyl-N-(alkylthio) aminyl radicals (2), $R_1 NSR_2$, were generated by hydrogen-atom abstraction from N-(alkylthio)alkylamines and were studied by electron spin resonance (ESR) spectroscopy. When both R_1 and R_2 in 2 were tert-alkyl, the corresponding radicals were extremely persistent in oxygen-free hydrocarbon solvents and showed no tendency to dimerize even at low temperatures. In the ESR signal of t-BuNSBu-t radical the satellite (5.93 G) due to ³³S in natural abundance could be detected. From a plot of ³³S hyperfine splitting (hfs) constants for three N-thioaminyl radicals vs. the π -spin densities on the sulfurs of the radicals calculated by the Hückel method or McLachlan perturbation treatment, a magnitude of 23 G for Q_s of the McConnell type equation ($a = Q\rho^{\pi}$) was obtained. Ab initio molecular orbital calculations on a model radical, HNSH, with the double-zeta basis set predicted a trans-coplanar structure as the most stable conformation.

Introduction

Recently, a variety of N-alkoxy-N-alkylaminyl radicals (3), $R_1 NOR_2$, have been widely studied by electron spin resonance (ESR) spectroscopy.²⁻⁴ The generation was achieved by photolysis of R₁NHCOOOBu-t and R₁NHOR₂, and oxidation of R₁NHOR₂ with inorganic oxidizing agents. It was found that INDO molecular orbital calculations on CH₃NOCH₃ radical predicted a trans-coplanar structure as the most stable conformation² and that, when R_1 and \mathbf{R}_2 in 3 were both *tert*-alkyl, the corresponding radicals showed no tendency to dimerize and persisted in oxygenfree conditions with no detectable decay.⁴

⁽²⁰⁾ In view of the consistency between the crystallographic data^{3,4} and the electronic absorption and emission spectroscopy^{6,1} for the proposed intrazeolitic guests, Ag^0 , $Ag_2^{q^+}$, and $Ag_3^{p^+}$ it is surprising that, on one hand, there is no observable EPR signal attributable to these paramagnetic species (at least Ag_1^0 , the charges p and q for Ag_2^{q+} and Ag_3^{p+} being not precisely known) and, on the other hand, considering the extensive previous EPR work done, that no spectra have been reported for the vacuum dehydrated forms of AgNa-X and AgNa-Y zeolites. Note that the EPR spectra of similar species $(Ag_1^0 \text{ and } Ag_{n+1}^n \text{ for } n = 1, 2, 3 ...)$ have been observed in hydrated or partially dehydrated silver exchanged zeolites A, X, Y following γ - or X-ray irradiation.²⁶⁻¹⁷ The EPR silence for the species may be due to several factors, such as, saturation of the paramagnetic species at low microwave powers at the recording temperature, due to spin-lattice relaxation effects, coupled with broadening effects due to the existence of other paramagnetic species in the vicinity of the silver guests.

⁽²¹⁾ G. A. Ozin, F. Hugues, D. F. McIntosh, and S. M. Mattar in "Intrazeolite Chemistry", G. D. Stucky and F. G. Dwyer, Ed., American Chemical Society, Washington, DC, 1983, ACS Symp. Ser., No. 218, p 409; J. Phys. Chem., manuscript in preparation.

⁽¹⁾ Part 19 in the series "ESR Studies of Nitrogen-Centered Free Radicals". For part 18, see: Miura, Y.; Yamamoto, A.; Kinoshita, M. Bull.
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⁽⁴⁾ Woynar, H.; Ingold, K. U. J. Am. Chem. Soc. 1980, 102, 3813.

In contrast to the detailed ESR studies on 3, their sulfur analogues, N-alkyl-N-(alkylthio)aminyl radicals (2) have never appeared in the literature. The t-BuNSN(t-Bu)MRn radicals, reported by Ingold et al.,⁵ were the only structurally related radicals which were generated by the additions of transient radicals (RnM-) to di-tert-butylsulfur diimide. In a continuing study on N-thioaminyl radicals by ESR spectroscopy, we shot a light at the unreported radicals, $2.^6$ It was found that the radicals could be successfully generated by hydrogen-atom abstraction from N-(alkylthio)alkylamines (1) with tert-butoxyl radicals. The present work reports the first ESR studies on 2. Furthermore, we performed ab initio molecular orbital calculations on a model radical, HNSH, with the doublezeta basis set to obtain insight into the most stable conformation of 2.

Experimental Section

Infrared (IR) and ¹H nuclear magnetic resonance (NMR) spectra were measured as previously reported.⁷ Refractive indexes were taken on an Atago refractometer at 30 °C.

Materials. 2-Methyl-2-nitrosopropane⁸ and di-tert-butyl diperoxyoxalate⁹ were prepared by the reported methods. N-Thioamines 1 were prepared as follows:

N-(Isopropylthio)-tert-butylamine (1a). A stream of chlorine was bubbled into a solution of 2-propanethiol (10.0 g, 0.129 mol) in dry hexane (50 mL) at 25 ± 3 °C for 30-50 min,¹⁰ the hexane solution turning orange. After the excess chlorine was removed by bubbling nitrogen for 15 min, the hexane solution was added dropwise to a stirred solution of tert-butylamine (21 g, 0.29 mol) in dry diethyl ether (ether) (400 mL) at 0-5 °C. After being stirred for 1 h at the same temperature, the reaction mixture was filtered, evaporated, and distilled at $50-58 \text{ }^{\circ}\text{C}/19$ torr to afford a colorless oil in 30% yield (5.6 g), which was further distilled at 60-61 °C/18 torr: IR (neat) 3290 cm⁻¹ (NH); n^{30} _D 1.4458; ¹H NMR (CCl₄) δ 1.10 (s, *t*-Bu, 9 H), 1.15 (d, J =7 Hz, CHMe₂, 6 H), 2.43 (br s, NH, 1 H), and 2.75 (sept, J = 7 Hz, CHMe₂, 1 H). Anal. Calcd for C₇H₁₇NS: C₂ 57.08; H, 11.64; N, 9.51. Found: C, 57.00; H, 11.64; N, 9.59.

N-(*Butylthio*)-*tert-butylamine* (1*b*). A hexane solution of butanesulfenyl chloride, prepared from 10.0 g (0.111 mol) of butanethiol in the same manner as described above, was added to a stirred solution of *tert*-butylamine (17 g, 0.23 mol) in dry ether (400 mL) at 0–5 °C. After being stirred for 1 h at the same temperature, the reaction mixture was filtered, evaporated, and distilled at 45–46 °C/2.5 torr to afford a colorless oil in 12% yield (2.2 g). An analytical sample was obtained by further distillation at 58–59 °C/4.5 torr: IR (neat) 3300 cm⁻¹ (NH); n^{30}_{D} 1.4510; ¹H NMR (CCl₄) δ 0.79–1.90 (m, CH₃CH₂CH₂, 7 H), 1.09 (s, *t*-Bu, 9 H), ca. 2.4 (br s, NH, 1 H), and 2.45 (t, *J* = 7 Hz, SCH₂, 2 H). Anal. Calcd for C₈H₁₉NS: C, 59.56; H, 11.87; N, 8.68. Found: C, 59.79; H, 11.97; N, 8.44.

N-(*tert-Butylthio*)-*tert-butylamine* (1c). A stream of chlorine was bubbled into a solution of *tert*-butyl disulfide (9.5 g, 0.053 mol) in dry hexane (50 mL) at 30 ± 3 °C for 30–50 min,¹⁰ the hexane solution turning orange. After the excess chlorine was removed by bubbling nitrogen for 15

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- **1960**, 82, 1762.
- (10) Himel, C. M. U.S. Patent 2807615, 1957.

min, the hexane solution was added dropwise to a stirred solution of *tert*-butylamine (21 g, 0.28 mol) in dry ether (400 mL) at 0–5 °C. After being stirred for 1 h at the same temperature, the reaction mixture was filtered, evaporated, and distilled at 53–54 °C/10 torr to afford a colorless oil in 34% yield (5.7 g). An analytical sample was obtained by further distillation at 30–31 °C/2.0 torr: IR (neat) 3270 cm⁻¹ (NH); $n^{30}_{\rm D}$ 1.4470; ¹H NMR (CCl₄) δ 1.12 (s, *t*-Bu, 9 H), 1.16 (s, *t*-Bu, 9 H), and 2.52 (br s, NH, 1 H). Anal. Calcd for C₈H₁₉NS: C, 59.56; H, 11.87; N, 8.68. Found: C, 59.63; H, 11.80; N, 8.95.

N-(tert-Butylthio)-1-adamantanamine (1d). A hexane solution of 2-methyl-2-propanesulfenyl chloride, prepared from 5.0 g (0.028 mol) of tert-butyl disulfide, was added dropwise to a stirred solution of 1-adamantanamine (4.2 g, 0.028 mol) and triethylamine (5 mL) in dry ether (250 mL) at 0-5 °C. After being stirrerd for 2 h at the same temperature, the reaction mixture was filtered and evaporated, and the residue was chromatographed on silica gel (Wacogel C-200) with benzene-hexane (1:5) as eluant to give 1d as a colorless viscous oil in 25% yield (1.7 g): IR (neat) 3250 cm⁻¹ (NH); ¹H NMR (CCl₄) δ 1.14 (s, t-Bu, 9 H), 1.62-2.02 (m, adamantyl, 15 H), and 2.42 (br s, NH, 1 H). Elemental analysis did not give satisfactory results.

N-(Cyclohexylthio)-tert-butylamine (1e). A hexane solution of cyclohexanesulfenyl chloride, prepared from 10 g (0.086 mol) of cyclohexanethiol in the same manner as for 2-propanesulfenyl chloride, was added dropwise to a stirred solution of tert-butylamine (14 g, 0.19 mol) in dry ether (400 mL) at 0-5 °C. After being stirred for 1 h at the same temperature, the reaction mixture was filtered, evaporated, and distilled at 53-60 °C/0.06 torr to afford a colorless oil in 27% yield (4.4 g). An analytical sample was obtained by further distillation at 59-60 °C/0.06 torr: IR (neat) 3280 cm⁻¹ (NH); n^{30}_{D} 1.4838; ¹H NMR (CCl₄) δ 0.90-2.30 (m, cyclohexyl, 11 H), 1.10 (s, t-Bu, 9 H), and 2.41 (br s, NH, 1 H). Anal. Calcd for C₁₀H₂₁NS: C, 64.11; H, 11.30; N, 7.48. Found: C, 64.26; H, 11.60; N, 7.71.

N-[(Trichloromethyl)thio]-tert-butylamine (1f). If was prepared by the method of Glass¹¹ and purified by distillation at 77–79 °C/1.7 torr (lit.¹¹ 45 °C/0.08 torr): IR (neat) 3350 cm⁻¹ (NH); n^{30}_{D} 1.5029. Anal. Calcd for $C_5H_{10}Cl_3NS$: C, 26.98; H, 4.53; N, 6.29. Found: C, 27.02; H, 4.54; N, 6.33.

N-(tert-Butylthio)methylamine (1g). 1g was prepared from 9.5 g (0.053 mol) of tert-butyl disulfide and ca. 10 g (0.32 mol) of methylamine by the same method as for 1c and purified by distillation at 53–54 °C/42 torr: yield 10% (1.2 g); IR (neat) 3290 cm⁻¹ (NH); n^{30}_{D} 1.4502; ¹H NMR (CCl₄) δ 1.20 (s, t-Bu, 9 H), 2.24 (br s, NH, 1 H), and 2.77 (d, J = 6 Hz, CH₃, 3 H). Anal. Calcd for C₅H₁₃NS: C, 50.37; H, 10.99; N, 11.75. Found: C, 50.47; H, 11.09; N, 11.38.

N-(tert-Butylthio)ethylamine (1h). 1h was prepared from 9.5 g (0.053 mol) of tert-butyl disulfide and 12 g (0.27 mol) of ethylamine by the same method as for 1c and purified by distillation at 60–61 °C/30 torr: yield 20% (2.8 g); IR (neat) 3290 cm⁻¹ (NH); n^{30} _D 1.4469; ¹H NMR (CCl₄) δ 1.10 (t, J = 7 Hz, CH₃, 3 H), 1.18 (s, t-Bu, 9 H), 2.22 (br s, NH, 1 H), and 2.93 (quint, J = 7 Hz, CH₂, 2 H). Anal. Calcd for C₆H₁₆NS: C, 54.08; H, 11.35; N, 10.51. Found: C, 53.98; H, 11.39; N, 10.66.

N-(tert-Butylthio)isopropylamine (1i). 1i was prepared from 9.5 g (0.053 mol) of tert-butyl disulfide and 15 g (0.25 mol) of isopropylamine by the same method as for 1c and purified by distillation at 60–61 °C/24 torr: yield 34% (5.3 g); IR (neat) 3290 cm⁻¹ (NH); n^{30} _D 1.4442; ¹H NMR (CCl₄)

⁽⁵⁾ Brunton, G.; Taylor, J. F.; Ingold, K. U. J. Am. Chem. Soc. 1976, 98, 4879.

⁽⁶⁾ For a preliminary communication of this work, see: Miura, Y.; Asada, H.; Kinoshita, M. Chem. Lett. 1978, 1085.

⁽⁷⁾ Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. J. Org. Chem. 1980, 45, 3875.

⁽¹¹⁾ Glass, R. S.; Swedo, R. J. Synthesis 1977, 798.

TABLE I: ESR Parameters for N-Alkyl-N-(alkylthio)aminyls (R_1NSR_2) and Related Radicals^{*a*,*b*}

	R ₁	R ₂	temp, °C	a _N	а _{β-Н}	^a SCH	g	method ^c
2a	t-Bu	<i>i</i> -Pr	15	12.35		3.53 (1 H)	2.0075	а
2b	t-Bu	n-Bu	15	12.13		3.09 (2 H)	2.0075	а
2c	t-Bu	t-Bu	15	12.44		. ,	2.0073	a, b
$2\mathbf{c}^d$			23	12.37			2.0074	b
$2c^d$			-30	12.34			2.0074	b
$2\mathbf{c}^d$			-70	12.28	$6.2 (^{13}C), ^{e} 5.93 (^{33}S)$		2.0074	b
2d	1-ada ^f	t-Bu	24	12.40			2.0074	а
2e	t-Bu	c-Hx	15	12.25		3.05(1H)	2.0075	а
2f	t-Bu	CCl.	15	12.91		x ,	2.0061	а
2g ^g	Me	t-Bu	-60	12.5	16.4 (3 H)			b
$\overline{2h}$	Et	t-Bu	40	12.4	15.2(2H)		2.0073	a
$2\mathbf{h}^{h}$			-22	12.37	15.08(2H)		2.0075	b
$2\mathbf{h}^{h}$			-42	12.28	15.14(2 H)		2.0075	b
$2\mathbf{h}^{h}$			-72	12.24	15.25 (2 H)		2.0075	Ď
2i	<i>i</i> -Pr	t-Bu	15	12.41	9.08 (1 H)		2.0073	a
2i	n-Bu	t-Bu	15	12.38	15.37(2 H)		2.0073	a
_, 2k	c-Hx	t-Bu	15	12.34	9.08(1 H)		2 0073	a
4a	t-BuN(O)SEt	20	18.08	0.00 (1 11)		2.0070	u
4b	t-BuN(O	()SPr-i	$\overline{20}$	17 14			2,0069	
40	t-BuN(O	SBu-n	$\overline{20}$	18 28			2.0000	
4d	t-BuN(O	\cdot)SBu-t	20	15.42			2.0067	

^a Hyperfine splitting constants are given in gauss. ^b Solvent: benzene unless otherwise stated. ^c Method of generation of radicals. ^d t-BuNHSBu-t:t-BuOOBu-t:hexane = 1:1:10 (in vol). ^e Assigned to the *N*-tert-butyl quaternary carbon. ^f 1-Adamantyl. ^g MeNHBu-t:t-BuOOBu-t:hexane = 1:1:3 (in vol). ^h EtNHSBu-t:t-BuOOBu-t:hexane = 1:1:2 (in vol).

δ 1.08 (d, J = 6 Hz, CHMe₂, 6 H), 1.17 (s, t-Bu, 9 H), 2.25 (br s, NH, 1 H), and 2.95 (sept, J = 6 Hz, CHMe₂, 1 H). Anal. Calcd for C₇H₁₇NS: C, 57.08; H, 11.64; N, 9.51. Found: C, 56.87; H, 11.58; N, 9.80.

N-(tert-Butylthio)butylamine (1j). 1j was prepared from tert-butyl disulfide and butylamine by the same method as for 1c. However, purification by distillation resulted in decomposition of the desired amine. For ESR measurement, the concentrate of the reaction mixture was employed.

N-(*tert-Butylthio*)*cyclohexylamine* (1*k*). 1*k* was prepared from 9.5 g (0.053 mol) of *tert*-butyl disulfide and 25 g (0.25 mol) of cyclohexylamine by the same method as for 1c and purified by distillation at 53–54 °C/0.08 torr (lit.¹² 57–58 °C/1 torr): yield 30% (6.0 g); IR (neat) 3270 cm⁻¹ (NH); $n^{30}_{\rm D}$ 1.4831 (lit.¹² $n^{20}_{\rm D}$ 1.4870); ¹H NMR (CCl₄) δ 1.10–2.70 (m, cyclohexyl, 11 H), 1.17 (s, *t*-Bu, 9 H), and 2.31 (br s, NH, 1 H). Anal. Calcd for C₁₀H₂₁NS: C, 64.11; H, 11.30; N, 7.48. Found: C, 63.99; H, 11.24; N, 7.34.

Generation of Radicals. Aminyl radicals 2 were generated by (a) thermolysis of a mixture of 1 (30 mg) and di-tert-butyl diperoxyoxalate (20 mg) in degassed benzene solution (0.20 mL) and (b) direct photolysis of a degassed benzene or hexane solution containing 1 and di-tert-butyl peroxide in the ESR cavity with a 100-W (JEOL-UV-1) or 500-W (Ushio ES-UV-5H) super high-pressure mercury lamp. Alkyl alkylthio nitroxide radicals (4) were generated by the reaction of alkanethiols (0.1–0.2 mL) with di-tertbutyl diperoxyoxalate (5–10 mg) in degassed benzene solution in the presence of 2-methyl-2-nitrosopropane (10–30 mM). N,N-Bis(tert-butylthio) (3,5-di-tert-butylphenyl)aminyl radical (9) was generated by the previously reported method.¹⁴ The satellites detected are $a_{^{33}S} = 4.66$ G, $a_{^{13}C}$ = 5.20 and 10.20 G (benzene, 17 °C).

ESR measurements were carried out with a JEOL JES-ME-3X spectrometer, equipped with an X-band microwave unit and 100-kHz field modulation. Temperature control was performed with a JEOL JES-VT-3 apparatus. Hyperfine splitting (hfs) constants and g values



Figure 1. ESR spectrum of *N*-isopropyl-*N*-(*tert*-butylthio)aminyl radical (2) from the reaction of *N*-(*tert*-butylthio)isopropylamine (1) with di*tert*-butyl diperoxyoxalate in benzene at 15 °C.

were determined by comparison with those $(a_N = 13.09 \text{ G}, g = 2.0057)$ for Fremy's salt in K₂CO₃ aqueous solution.

Results

N-Thioaminyl radicals 2 were generated by (a) the re-

action of 1 with di-tert-butyl diperoxyoxalate and (b) photolysis of 1 in the presence of di-*tert*-butyl peroxide. Method a usually gave relatively strong ESR signals of 2, as found in Figure 1. However, for 1g and 1h the observed ESR signals were very weak. In the cases of 1a and 1b, two kinds of ESR signals in the intensity ratio of 1:1-3 were concurrently observed with partial overlapping. The weaker signal of the two was identified as 2a or 2b based on their ESR parameters. The other stronger signal with a g value of 2.0051 was constituted of a 1:1:1 triplet with an interval of 14.11 G and was very persistent. This radical was also observed upon photolysis of N-(arylthio)-tertbutylamines in the presence of di-tert-butyl peroxide¹³ and was assigned to N-tert-butoxy-N-tert-butylaminyl based on its ESR parameters. Recently, Ingold et al. generated this radical unequivocally by hydrogen-atom abstraction from t-BuNHOBu-t, e.g., with inorganic oxidizing agents

⁽¹²⁾ Himel, C. M.; Edmonds, L. O. U.S. Patent 2520400, 1950.
(13) Miura, Y. Asada, H.; Kinoshita, M. Bull. Chem. Soc. Jpn. 1977, 50, 1855.

⁽¹⁴⁾ Miura, Y.; Asada, H.; Kinoshita, M. Bull. Chem. Soc. Jpn. 1980, 53, 720.

such as PbO₂, and gave the identical a_N value (14.1 G) for this radical.⁴

We also attempted to generate 2 by oxidation with PbO_2 or Ag_2O . However, the radical concentrations obtained were extremely low, even in the case of 2c. Thus, it was found that this method was quite unsuitable for the generation of 2.

As had been anticipated, when both R_1 and R_2 in 2 were tert-alkyl, the corresponding radicals (2c and 2d) were very persistent. For example, in the case of 2c photolysis of a 0.5 M benzene solution of 1c containing 10% di-tertbutyl peroxide gave a 10⁻³ M radical solution, and this radical, after interruption of the UV irradiation, persisted for more than 1 day ($\tau_{1/2}$: ~10 h at 15 °C). However, when air was bubbled into the radical solution, the radical concentration was rapidly reduced. In contrast to this high reactivity of 2 toward oxygen, aromatic N-thioaminyl radicals such as ArNSAr,⁷ t-BuNSAr,¹³ and ArNSBu-t¹⁴ persisted even in the presence of oxygen, as previously reported. The aromatic N-thioaminyl radicals are obviously more stabilized than 2 owing to the presence of benzene ring(s) in the π system. On the other hand, for 2 such a stabilization cannot be expected. The high reactivity of 2 toward oxygen may be attributable to this difference.

Radical 2c showed no sign of dimerizing even at low temperature. Usually, when solutions of radicals in equilibria with the dimers are cooled to low temperatures, the ESR signal intensities are remarkably reduced owing to the preferred dimer formation of the radicals. However, in the case of 2c the ESR signal intensity was increased with lowering of temperature.¹⁵ This behavior of this radical obviously reveals no tendency to dimerize in solution even at low temperature. We consider this is due to the large crowd of atoms around the radical center.

It is well-known that the detection of satellites due to ³³S in natural abundance (0.74%) is generally very difficult because the intensity of the ³³S satellites is theoretically only 0.19% of that of the parent line ($m_I = 3/2$). However, if high radical concentration solutions are obtained, one may be permitted to observe the satellites. Radical 2c is just the case. However, the relatively broad lines (the peak-to-peak line width, ca. 2.7 G at room temperature) prevented detection of the ³³S satellite. Fortunately, however, when the radical solution was cooled to -70 °C, the line width was reduced to ca. 1.0 G and this reduction in the line width permitted us to measure the satellite (5.93 G) due to ³³S, together with the satellite (6.2 G) due to ¹³C.

Discussion

ESR Parameters. The a_N values for 2 are almost constant (12.13–12.91 G), regardless of the bulkiness of alkyl groups, and are very close to those (12.0–12.6 G) for t-BuNSN(t-Bu)MRn radicals.⁵ It is obvious from Table I that the magnitudes of these values are quite different from those for alkyl alkylthio nitroxide radicals (4), gen-

$$\operatorname{RSH} \xrightarrow{(t-\operatorname{Bu}OOCO)_2} \operatorname{RS} \cdot \xrightarrow{t-\operatorname{Bu}NO} t-\operatorname{Bu}N(O \cdot)\operatorname{SR}$$

erated by the additions of alkylthiyl radicals to 2methyl-2-nitrosopropane.¹⁶ Thus, we can safely rule out the possibility that the radicals found in this work are not 4. The relatively large g values found for 2 are obviously attributable to the considerable delocalization of the unpaired electron onto the sulfur having a large spin-orbit coupling parameter.^{17,18} The smaller a_N values for 2 compared with those (13.95–14.5 G) for R₁NOR₂ radicals²⁻⁴ can be reasonably explained by the larger ability of sulfur groups to remove the unpaired electron than that of oxygen groups.¹⁹ This is further supported by the $a_{\beta-H}$ values for 2 smaller than those for R₁NOR₂ radicals (e.g., for 2g, 16.4 G and for H₃CNOBu-t,² 21.51 G) and by the a_{SCH} values for 2 larger than the a_{OCH} values for the latter radicals (e.g., for 2b, 3.09 G and for EtNOEt,² 2.50 G).

As found in Table I, the magnitude of the a_N value for **2f** is somewhat larger than those for the other **2** and its g value is smaller. This can be reasonably interpreted by the less importance of the contribution of the dipolar canonical structure B compared with the case of the others,

$$\begin{array}{c} R_1 - \dot{N} - \ddot{S} - R_2 \rightleftharpoons R_1 - \ddot{N}^- - \dot{S}^+ - R_2 \\ A \end{array}$$

probably owing to the presence of a strong electron-withdrawing substituent, trichloromethyl group.

In contrast to the almost similar values of a_N for 2, the magnitudes of the $a_{\beta-H}$ values vary widely, being dependent on both the spin density (ρ) on the nitrogen and the time-average dihedral angle (θ) between the β -hydrogen and $2p_z$ orbital on the nitrogen, as represented by the following equation:²⁰

$$a_{\beta-H} = \rho_{\rm N}(A + B\cos^2\theta) \simeq \rho_{\rm N}B\cos^2\theta = 32.8\cos^2\theta \quad (1)$$

where A and B are constants and A can generally be neglected. Since the ρ_N value can be taken as constant from the almost similar a_N values for 2 and a freely rotating methyl group exhibits $\theta = 45^{\circ}$, we can determine the $\rho_{\rm N}B$ to be 32.8 G based on the $a_{\beta-H}$ value of 16.4 G for 2g. The θ values calculated for 2h (R₁ = Et) and 2j (R₁ = n-Bu) are 47° and those for 2i ($R_1 = i$ -Pr) and 2k ($R_1 = cyclo$ hexyl) are 58°. In the case of 2h the a_{β} -H value is almost constant over the temperature range of 40 to -72 °C, revealing that the ethyl group almost freely rotates even at -72 °C. This is in contrast to the result found for EtNOBu-t radical² for which the $a_{\beta-H}$ value is increased 2.2 G upon cooling to -80 °C. The finding that the ethyl group of 2h freely rotates even at -72 °C can be interpreted in terms of the negligible steric interaction between the ethyl and t-butyl groups, probably owing to the relatively large N-S and C-S bond distances in 2. Similarly, the butyl group in 2j rotates freely at 15 °C. The θ value of 58° found for 2i and 2k is greater than 45° and lies in the range of the values (52-68°) reported for nitrogen-centered free radicals in π ground states.²¹

Ab Initio Molecular Orbital Calculations. In order to obtain insight into the most stable conformation for 2, ab initio molecular orbital calculations on a model radical, HNSH, were performed with the double-zeta basis set using the Gaussian 70 program. The total energies and hyperfine splitting (hfs) constants were calculated by the pseudoorbital theory.²²

In the present calculations, the bond lengths of N–H and S–H and the bond angles of H–N–S (θ_1) and H–S–N (θ_2)

⁽¹⁵⁾ Relative integrated ESR signal intensities measured in hexane at 10 and -70 °C, and again at 10 °C were 1.00, 1.36, and 0.965, respectively.

⁽¹⁶⁾ Some alkylthio tert-butyl nitroxide radicals have already appeared in the literatures; for example, see: Joshi, A.; Yang, G. C. J. Org. Chem. 1981, 46, 3736 and references cited therein.

 ⁽¹⁷⁾ Sulfur spin-orbit coupling parameter is 382 cm⁻¹; McClure, D. S. J. Chem. Phys. **1949**, 17, 905.

⁽¹⁸⁾ Danen, W. C.; Neugebauer, F. A. Angew. Chem., Int. Ed. Engl. 1975, 14, 783.

⁽¹⁹⁾ Block, E. "Reactions of Organosulfur Compounds"; Blomquist, A. T.; Wasserman, H. H., Eds.; Academic Press: New York, 1978; p 189, 1978; p 189, p

 ⁽²⁰⁾ Heller, C.; McConnell, M. H. J. Chem. Phys. 1960, 32, 1535.
 (21) Danen, W. C.; Gellert, R. W. J. Am. Chem. Soc. 1980, 102, 3264.
 (22) (a) Nakatsuji, H.; Hirao, K. J. Chem. Phys. 1978, 68, 2053. (b) Ibid. 1978, 68, 4279. (c) Ohta, K.; Nakatsuji, H.; Hirao, K.; Yonezawa, T. Ibid. 1980, 73, 1770.



Figure 2. Optimized geometry of HNSH radical: bond lengths are given in angstroms and bond angles in degrees.



Figure 3. Potential curve calculated as a function of the dihedral angle θ_3 for the barrier to internal rotation.

were fixed,²³ and the N-S bond length and dihedral (torsion) angle (θ_3) were varied. The calculations yielded a trans-coplanar structure as the most stable conformation, as illustrated in Figure 2, and the unpaired electron occupied a π^* molecular orbital. Interestingly, this transcoplanar structure agrees well with the experimental geometry of [(4-nitrophenyl)thio](2,4,6-tri-tert-butylphenyl)aminyl radical crystal determined by the X-ray crystallographic analysis,²⁵ in which the N (central) and S atoms, and the S-benzene ring are all in the same plane and the two benzene rings are trans to each other. Furthermore, this structure is similar to that (trans-coplanar) for CH₃NOCH₃ radical predicted by the INDO calculations.²

The hfs constants calculated for this conformation are $a_{\rm H_1} = -24.13$, $a_{\rm H_2} = -3.14$, $a_{\rm N} = 10.68$, and $a_{^{33}\rm S} = 5.17$ G, which are in good agreement with experiment (e.g., for 2c in hexane at -70 °C, $a_{\rm N} = 12.28$ and $a_{^{33}\text{S}} = 5.93$ G). As found in Figure 3, the cis-coplanar structure is 1.5 kcal/mol more destabilized in the total energy than the trans-coplanar form. The hfs constants calculated for this cis form are $a_{\rm H_1} = -23.36$, $a_{\rm H_2} = -3.47$, $a_{\rm N} = 10.29$, and $a_{^{33}S} = 3.66$ G. Furthermore, the energy barrier to rotation about the N-S bond was calculated to be 9.8 kcal/mol. This relatively higher barrier to rotation compared with those for the ordinary single bonds²⁶ can be reasonably interpreted

TABLE II: Total Energies for Various Transition States

state		total energy, au	rel energy diff, kcal/mol
H-N	trans-coplanar	-452.988 885 5	0
H ≁ ŇS∕ ^{−H} 5	$\theta_3 = 90^{\circ} b$	-452.973 299 3	9.8

$$\theta_{1} = 180^{\circ b} -452.9324926 35.4$$

$$\theta_2 = 180^{\circ b} -452.8543722$$
 84.4
7

^a 1 au of energy (hartree) = 27.21 eV = 627.7 kcal/mol. ^b Geometric parameter different from those for the transcoplanar form.

TABLE III: ³³S Hfs Constants for 2c and Other N-Thioaminyl Radicals^a

N-thioaminyl	a _N	a ³³ N	g	
NSC ₆ D ₅	9.52	4.62	2.0060	
8 ^b 	9.93	4.66	2.0065	
t-BuNSN $(t$ -Bu)SiR ₃	12.0	8.34	2.0064	
t-BuNSBu-t	12.28	5.93	2.0074	
PhSNSPh 11 ^e	11.41	3.9	2.0075	

^a Hyperfine splitting constants are given in gauss. ^b Taken from ref 7. ^c The a_N and g values are taken from ref 14, and for the a^{33} solutions will be a set the Experimental Section in this issue. ^d Taken from ref 5. ^e Taken from ref 28. Also, see: Rolfe, S.; Griller, D.; Ingold, K. U.; Sutcliffe, L. H. J. Org. Chem. 1979, 44, 3515.

in terms of the formation of a three-electron bond between the nitrogen and sulfur, in which two of the three electrons are in a bonding orbital and the third is in an antibonding orbital.27

There are three possible paths to isomerization between the trans and cis forms for 2: (a) rotation about the N-S bond, (b) in-plane inversion at nitrogen, and (c) in-plane inversion at sulfur. In order to establish which pathway is the energetically most favorable to the isomerization, the total energies for the conformations (6 and 7) of the transition states on paths b and c were calculated. The results are shown in Table II. The energy barriers relative to the most stable (trans-coplanar) conformation are 9.8 kcal/mol for path a, 35.4 kcal/mol for path b, and 84.4 kcal/mol for path c, revealing that path a (rotation) is the energetically most favorable to the isomerization.

⁽²³⁾ The bond lengths of N-H (1.063 Å) and S-H (1.350 Å) are taken from the experimental data for NH_3 and H_2S molecules,²⁴ while the bond angles of H–N–S (114.4°) and H–S–N (103.1°) are based on the data of the X-ray crystallographic analysis for [(4-nitrophenyl)thio](2,4,6-tri-tert-butylphenyl)aminyl radical crystal.²⁵

⁽²⁴⁾ Sutton, L. E. Chem. Soc., Spec. Publ. 1965, No. 2.
(25) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M.; Sato, S.; Tamura, C. J. Org. Chem. 1982, 47, 2618.

wieser, A., Jr., Taft, R. W., Eds.; Wiley-Interscience: New York, 1968; Vol. 6, pp 1-80.

⁽²⁷⁾ Baird, N. C. J. Chem. Educ. 1977, 54, 291.

Radicals 2 probably rotate freely around the N-S bond at room temperature, judged by the rotational barrier of 9.8 kcal/mol. However, the time-average ESR signal may diverge into two signals due to the cis and trans forms on decreasing the temperature. However, this separation of the ESR signal was never found even at -80 °C. This is probably due to very similar magnitudes of the a_N values for both forms, as predicted by the ab initio molecular orbital calculations.

³³S Hfs Constants. It is usually very difficult to estimate experimentally the π -spin density on sulfur unless ³³S hfs can be detected. Fortunately, we have successfully detected ³³S hfs's for some N-thioaminyl radicals,^{7,28} including 2c, without any enrichment of ³³S atoms. The results are summarized in Table III, together with the a_{33S} value reported for t-BuNSN(t-Bu)SiR₃ radicals.⁵

Following the treatment developed by Karplus and Fraenkel for ¹³C hfs's,²⁹ we can obtain eq 2. for ³³S hfs's.

$$a_{^{33}S} = (S_s + \sum_i Q_{sx_i}{}^s) \rho_s{}^{\pi} + \sum_i Q_{x_i}{}^s \rho_{x_i}{}^{\pi}$$
(2)

Sullivan approximated this equation to the simple McConnell type equation in the system of nonplanar sulfide radical cations,³⁰ as well as for other nuclei such as ¹³C and ¹⁷O (eq 3). This equation was also supported

$$a_{^{33}\mathrm{S}} = Q_{_{\mathrm{B}}}\rho_{_{\mathrm{S}}}{}^{\pi} = 33\rho_{_{\mathrm{S}}}{}^{\pi} \tag{3}$$

by the system of planar radical cations.³¹ For the sulfur-nitrogen heterocyclic radical anion π system,³² however, the magnitude of 33 G for Q_s was not necessarily valid and a magnitude of 22 G was suggested from the simple analysis.

In order to estimate whether the magnitude of 33 G for $Q_{\rm s}$ of eq 3 is common or not, we derived the $Q_{\rm s}$ value, using the ^{33}S hfs constants found for the N-thioaminyl radicals. The π -spin density distributions were calculated with the standard Hückel method and McLachlan perturbation treatment,³³ assuming the radicals to be planar. This planar assumption is supported by the experimental geometry of [(4-nitrophenyl)thio](2,4,6-tri-tert-butylphenyl)aminyl radical crystal.²⁵ Moreover, the ab initio molecular orbital calculations described above predict a planar structure for 2. The parameters employed in this work, which are chosen on the basis of the literature values,^{31,32,34} are as follows: $\alpha_{\rm N} = \alpha + 0.6\beta$, $\alpha_{\rm S} = \alpha + \beta$, $\beta_{\rm CN} = 1.1\beta$, $\beta_{\rm NS} = 0.7\beta$, $\beta_{\rm CS} = 0.7\beta$, and $\lambda = 0.7.35$ As the parameters show, only the p-orbital model³⁶ for sulfur was considered in the present work, since good agreement with experimental values was found without considering the d orbitals.³⁷ The results are summarized in Table IV. As can be seen from the table, for 12 and 13 the McLachlan perturbation treatment gives good agreement with experiment, whereas for 11 the Hückel method gives better results. Thus, for 12 and 13 the results from the McLa-

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(33) McLachlan, A. D. Mol. Phys. 1960, 3, 233.
(34) (a) Strom, E. T.; Russell, G. A. J. Am. Chem. Soc. 1965, 87, 3326.
(b) Chiu, M. F.; Gilbert, B. C.; Hanson, P. J. Chem. Soc. B 1970, 1700.
(c) Haddon, R. C.; Kaplan, M. L.; Marshall, J. H. J. Am. Chem. Soc. 1978, 1000 (2010) 100, 1235 and references sited therein.

(35) Furthermore, the π -spin density distributions were calculated with an alternate set of parameters $(\alpha_N = \alpha + 1.1\beta, \alpha_S = \alpha + 1.3\beta, \beta_{CN} = 1.1\beta, \beta_{NS} = 0.7\beta, \beta_{CS} = 0.7\beta, and \lambda = 0.7)$. However, a very similar magnitude of Q_s (22 G) was also obtained. (36) Lucken, E. A. C. Theor. Chim. Acta 1963, 1, 397. (37) L.-Higgins, H. C. Trans. Faraday Soc. 1949, 45, 173.

TABLE IV: Calculated and Experimental Spin Density Distributions in N-Thioaminyl Radicals

M this sectors!	posi-	IIMO	Matashlan	amm+10
N-thioaminyl	tion	HMO	McLachlan	exptle
	1	0.375	0.470	0.436
	2	0.001	-0.043	
	3	0.114	0.140	0.137
125	4	0.000	-0.034	0.047
	5	0.114	0.131	0.155
	8	0.207	0.191	0.201 ^c
	9	0.000	-0.012	
	10	0.025	0.023	0.029
	11	0.000	-0.008	0.009
	12	0.025	0.021	0.031
4 3 8	1	0.408	0.492	0.451
(5 2)-N-S	2	0.001	-0.049	
	3	0.124	0.144	0.140
13 ^d	4	0.000	-0.037	0.047
	5	0.124	0.133	0.152
	8	0.219	0.211	0.203 ^e
	1	0.533	0.698	0.519
	2	0.167	0.116	0.170
	3	0.002	-0.005	
11/	4	0.022	0.017	0.021
	5	0.000	-0.006	
	6	0.022	0.018	0.021

^a Calculated from the McConnell equation, $a_x = Q_x \rho_x^{\pi}$, where $Q_{\rm H} = -27$, $Q_{\rm N} = 22$, $Q_{^{33}\rm S} = 23$ G. ^b Miura, Y.; Kinoshita, M. Bull. Chem. Soc. Jpn. 1977, 50, 1142. ^c Value for radical 8. ^d See, ref 14. ^e Value for radical 9. ^f See ref 28.

chlan perturbation treatment were employed, while for 11 the results from the Hückel method were employed in the following treatment.

For N-thioaminyl radicals, eq 2 can be rewritten as follows:

$$a_{^{33}\text{S}} = (S_{s} + Q_{\text{SN}}{}^{s} + Q_{\text{SC}}{}^{s})\rho_{s}{}^{\pi} + Q_{\text{NS}}{}^{s}\rho_{\text{N}}{}^{\pi} + Q_{\text{CS}}{}^{s}\rho_{c}{}^{\pi} \qquad (4)$$

Since $Q_{\rm CS}$ is very small $(1.8 \text{ G})^{30}$ and $\rho_c^{\pi} \approx 0$, the last term can be neglected. Letting $Q_s = (S_s + Q_{SN}^s + Q_{SC}^s)$, then

$$a_{^{33}\rm S}/\rho_{\rm N}{}^{\pi} = Q_{\rm s}\rho_{\rm s}{}^{\pi}/\rho_{\rm N}{}^{\pi} + Q_{\rm NS}{}^{\rm s} \tag{5}$$

From the least-squares treatment, we obtain $Q_s = 21.1$ and $Q_{\rm NS} = 0.8 \ (\gamma = 0.950)$, using the data in Tables III and IV. Since $Q_s \gg Q_{\rm NS}^s$, eq 4 can be approximated to the McConnell type equation, as well as in the case of the sulfide radical cations.³⁰ A plot of the ³³S hfs constants for 11–13 vs. the calculated π -spin densities gives $Q_s = 23$ G. From this result, it can be safely said that the magnitude of 33 G for Q_s of the McConnell type equation is not necessarily common. For N-thioaminyl radicals the value of 23 G should be employed. The π -spin density on the sulfur of 2c, estimated from eq 6, is 0.26, which yields

$$a_{33S} = Q_{s}\rho_{s}^{\pi} = 23\rho_{s}^{\pi} \tag{6}$$

the π -spin density of 0.74 on the nitrogen, provided that delocalization of the unpaired electron onto the alkyl groups can be neglected.

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Registry No. 1a, 68597-72-8; 1b, 68597-73-9; 1c, 68597-71-7; 1d, 86260-42-6; 1e, 51615-15-7; 1f, 65299-58-3; 1g, 41881-76-9; 1h, 68597-75-1; 1i, 68597-74-0; 1j, 86260-43-7; 1k, 68597-76-2; 2a, 68597-65-9; 2b, 68597-66-0; 2c, 68597-63-7; 2d, 86260-44-8; 2e, 68597-67-1; 2f, 68597-64-8; 2g, 86260-45-9; 2h, 68597-69-3; 2i, 68597-68-2; 2j, 86260-46-0; 2k, 68597-70-6; 4a, 58921-65-6; 4b, 58921-67-8; 4c, 58921-68-9; 4d, 78109-57-6; NNSH, 86260-47-1; di-tert-butyl diperoxyoxalate, 1876-22-8.