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Electron Spin Resonance Study of *N*-(Arylthio)alkylaminyl Radicals Generated by Photolysis of *N*,*N*-Bis(arylthio)alkylamines[1]

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A variety of *N*-(arylthio)alkylaminyl radicals (**2**), R$\dot{N}$SAr, were generated in solution by photolysis of *N*,*N*-bis(arylthio)alkylamines and were studied by electron spin resonance (ESR) spectroscopy. In the spectra of some **2**, satellites (5.75–6.7 G in benzene) due to ^{33}S in natural abundance could be found in the wings of the parent peaks. The large a_N (11.6–12.26 G) and large $a_{^{33}S}$ values for **2** showed that in **2** the unpaired electron resided mainly on the nitrogen and sulfur. When R in **2** was *tert*-alkyl, the corresponding **2** were quite long-lived in solution, even in the presence of oxygen. Since radicals **2** were found to exist in equilibrium with a dimer in solution, the enthalpies of dissociation of the dimers were estimated from the variation of the ESR signal intensity as a function of temperature to be 20.2–21.1 kcal/mol. The low enthalpies of dissociation were discussed in terms of the structures of the radicals and dimers.

Radical persistence is a function of electronic delocalization and steric protection.[2] Since *N*-thioaminyl radicals are electronically stabilized to a great extent by the conjugative electron delocalization with the lone pair of electrons on sulfur, if the reaction sites in the radicals are effectively protected by bulky groups, they can be largely expected to be made very persistent by this protection. In fact, we have found some *N*-thioaminyl radicals can be isolated as a hydrazine-type dimer[3] (**7**) which dissociates into the original radicals on dissolution at room temperature or as radical crystals whose structure has been defined by the X-ray crystallographic study.[4]

In the presence report we describe an electron spin resonance (ESR) spectroscopic study on *N*-(arylthio)alkylaminyl radicals (**2**) which have never been studied in detail.[5,6]

$$\underset{\mathbf{1}}{\mathrm{RN(SAr)_2}} \qquad \underset{\mathbf{2}}{\mathrm{R\dot{N}SAr}}$$

Although radicals **2** could be generated by UV photolysis of RNHSAr compounds alone,[5] the radical concentrations thus obtained were very low (~10^{-6} M). Furthermore, the chemical and thermal instabilities of RNHSAr compounds[7] have prevented extensive ESR studies on **2**. However, recently these problems could nicely be overcome by the finding of photolysis of *N*,*N*-bis(arylthio)alkylamines (**1**).[1,8,9] The radical concentrations of **2** obtained by this method were usually 5 × 10^{-5} to 10^{-4} M. Further advantages of this method were the facility in preparating precursors **1**, which could be obtained by the reaction of alkylamines with 2 equiv of arenesulfenyl chlorides, and their chemical and thermal stabilities.[10]

Results

Radicals **2** were generated by photolysis of **1** in a carefully degassed solution with a high-pressure mercury lamp. A typical ESR spectrum is shown in Figure 1 and the ESR parameters are summarized in Table I.

The principal feature in the ESR spectra of **2**, having no β-hydrogen, is a 1:1:1 triplet due to the interaction with a nitrogen. In the spectra of **2g** and **2f**, having a β-hydrogen, the triplet was further split into a doublet with an interval of 9.1–9.2 G. As for the splittings due to the aromatic protons, they were generally considerably poor (when R was *tert*-butyl) or completely destroyed (when R was adamantyl). Therefore, these spectra were relatively broad. However, when either or both of the meta positions were substituted by chlorine atoms(s), the spectra became well resolved as found in Figure 1 and the peak-to-peak line widths became small. Thus, in the spectrum of **2k** satellites due to ^{33}S could be found in the wings of the parent peaks without any enrichment of ^{33}S atoms (see, Figure 1). Similarly, ^{33}S satellites could also be detected in the spectra of the deuteriated (**2b**) and polysubstituted radicals (**2n**) owing to the relatively small peak-to-peak line widths (ca. 1.2 G).

When R in **2** was isopropyl (**2f**) or cyclohexyl (**2g**), the corresponding radicals were quite transient and on interruption of photolysis the ESR signals disappeared immediately. This instability of these radicals is the well-known behavior for the radicals having β-hydrogen(s) which is easily abstracted by another molecule of radical. However, when R was *tert*-alkyl, the corresponding radicals were quite persistent in hydrocarbon solvents such as benzene and hexane. Upon irradiation with a high-pressure mercury lamp the ESR signal intensity was rapidly developed and the radical concentrations reached from 5 × 10^{-5} to 10^{-4} M. Interestingly, on interruption of the photolysis the radical concentrations were still kept almost constant.[11] A brief kinetic study showed that the half-life times ($\tau_{1/2}$) of the *tert*-alkylaminyl radicals (**2a–e** and **2h–n**) at 16 °C in benzene solution were more than 10 h. In ethanol and

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[1] Part 21 in the seris "ESR Studies of Nitrogen-Centered Free Radicals". For part 20, see: Miura, Y.; Kunishi, T.; Kinoshita, M. *Chem. Lett.* **1983**, 885.

[2] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

[3] Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875.

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[5] Miura, Y.; Asada, H.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1855.

[6] Atkinson, R. S.; Awad, S. B.; Smith, E. A.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1976**, 22.

[7] The RNHSAr compounds having electron-donating substituents at the benzene ring were relatively unstable.

[8] Mayer, R.; Domschke, G.; Bleisch, S.; Bartl, A. *Tetrahedron Lett.* **1978**, 4003.

[9] Miura, Y.; Asada, H.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 720.

[10] Unless a strong electron-withdrawing substituent on the benzene ring was present, the RNHSAr compounds decomposed partly or completely on any silica or alumina column chromatogram, which we examined. However, compounds **1** showed no decomposition on such column chromatograms. Furthermore, although **1** in benzene was heated under reflux, no decomposition was revealed by TLC inspection.

[11] In the case of **2n** the radical concentration was rapidly reduced on interruption of photolysis. However, after ca. 10 min the radical concentration became constant.

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Table I. ESR Parameters for *N*-(Arylthio)alkylaminyl Radicals (2)[a]

	RṄSAr radical						
	Ar	R	temp, °C	solvent	a_N	a_{other}[b]	*g*
2a	C_6H_5	*t*-Bu	16	benzene	11.78	1.0 (3 H)[c]	2.0070
2b	C_6D_5	*t*-Bu	16	benzene	11.77	6.1 (^{33}S)	2.0070
2c	C_6H_5	ada[d]	16	benzene	11.73		2.0070
2d	$4\text{-}MeC_6H_4$	*t*-Bu	16	benzene	11.70	1.1 (5 H)[e]	2.0070
2e	$4\text{-}ClC_6H_4$	*t*-Bu	16	benzene	11.76	1.0 (2 H)[f]	2.0070
			16	hexane	11.78		2.0070
2f	$4\text{-}ClC_6H_4$	*i*-Pr	16	benzene	11.7	9.1 (1 H)[g]	
2g	$4\text{-}ClC_6H_4$	*c*-Hx	16	benzene	11.6	9.2 (1 H)[g]	
2h	$4\text{-}ClC_6H_4$	ada[d]	16	benzene	11.74		2.0070
2i	$3\text{-}ClC_6H_4$	*t*-Bu	16	benzene	11.84	1.09 (3H)[c]	2.0068
2j	$3\text{-}ClC_6H_4$	ada[d]	16	benzene	11.79		2.0068
2k	$3,5\text{-}Cl_2C_6H_3$	*t*-Bu	16	benzene	11.91	1.10 (3 H)[c] 5.80 (1 ^{13}C)[h] 5.75 (^{33}S)	2.0067
			24	hexane	11.95	1.08 (3 H)[c] 5.65 (^{33}S)	2.0067
			−10	hexane	11.98	1.08 (3 H)[c]	
			−31	hexane	11.95	1.08 (3 H)[c]	
			24	THF[i]	11.90	1.07 (3 H)[c]	2.0067
			24	$CHCl_3$	11.92	1.06 (3 H)[c]	2.0068
			24	ethanol	11.95	1.08 (3 H)[c]	2.0067
			24	CH_3CN	11.96	1.06 (3 H)[c]	2.0067
21	$4\text{-}BrC_6H_4$	*t*-Bu	16	benzene	11.82	1.1 (2 H)[f]	2.0072
2m	$4\text{-}BrC_6H_4$	ada[d]	16	benzene	11.76		2.0072
2n	$2,4,6\text{-}Me_3C_6H_2$	*t*-Bu	16	benzene	12.26	6.7 (^{33}S)	2.0076

[a] Hyperfine splitting constants are given in gauss. [b] Numbers in parentheses refer to number of equivalent nuclei. [c] Ortho and para protons. [d] 1-Adamantyl. [e] Methyl and ortho protons. [f] Ortho protons. [g] β-Proton. [h] Assigned to the *N*-*tert*-butyl quaternary carbon. [i] Tetrahydrofuran.

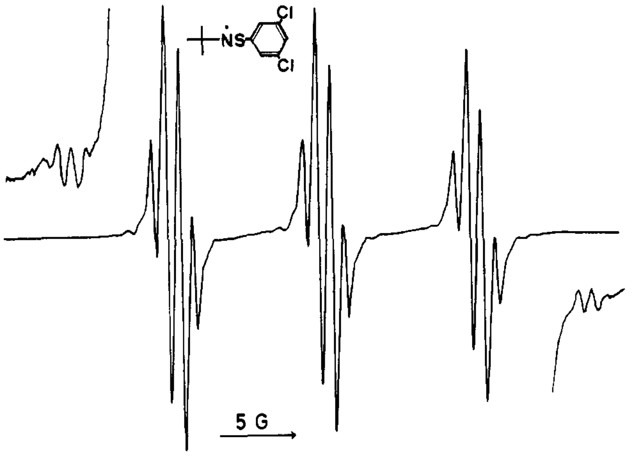
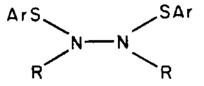


Figure 1. ESR spectrum of **2k** in benzene at 16 °C. The wings are shown under high amplification (100 times) and the ^{33}S satellite can be clearly seen.

tetrahydrofuran solutions the radicals also persisted ($\tau_{1/2}$ 2–4 h at 24 °C). However, in chloroform solution they did not persist; this is different from the cases in the other solvents. For example, the half-life time of **2a** was only 1 min at 24 °C and that of **2k** was 40 min at the same temperature.

We examined whether **2** reacted with oxygen or not. After the relative concentration of **2** in benzene solution in a degassed ESR cell was followed over 2 h as a function of time by measuring the area under the absorption curve of the integrated ESR signal, the cell was cut open and shaken vigorously for 3 min, and the relative radical concentration of **2** in the benzene solution exposed to air was followed for an additional 2 h by the same procedure. Interestingly, the radical persistence was not affected by air and from this result we concluded that **2** do not react with oxygen.

It was found that radicals **2** existed in equilibrium with a dimer in solution. When a toluene or hexane solution of **2** was cooled to −40 °C, the ESR signal became very weak or almost completely disappeared and, when the solution was raised to room temperature, the signal reappeared again and this cycle was completely reversible. The dimers can be almost undoubtedly identified as hydrazine **3** both by the high a_N values for **2** and by analogy to the previously isolated dimers (**7**) of *N*-(arylthio)-3,5-di-*tert*-butylphenylaminyl radicals.[3] Although we attempted to obtain the dimers by photolysis of **1** or by the reaction of *N*,*N*′-di-*tert*-butylhydrazine[12] with 2 equiv of arenesulfenyl chlorides, no dimers could be isolated from the reaction mixtures. In the former case the products identified by comparison of the R_f values with authentic samples were diaryl disulfides and RNHSAr. In the latter case only diaryl disulfides were isolated from the reaction mixtures.



3

Since the dimers are quite probably of the hydrazine type, the observation that radicals **2** exist in equilibrium with the dimers in solution at room temperature strongly suggests that the N–N bond of **3** is weak. The enthalpies of dissociation (Δ*H*) of the dimers were calculated from the slope of plots of ln *cT* vs. $^1/T$ according to the method of Vincow et al.,[13,14] where *c* is the relative radical concentration and *T* is the absolute temperature. The relative radical concentrations were estimated from (a) the value w^2h, where *w* is the peak-to-peak line width and *h* is the peak-to-peak amplitude of the ESR signal[13,15] and (b) the area under the absorption curve of the integrated ESR signal. The results are listed in Table II. As can be seen

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(15) The variations in peak-to-peak line width found between the temperature range 6 and 35 °C were 10% for **2a**, 17% for **2b**, and 2–4% for **2c**, **2h**, **2j**, and **2m**.

Table II. Enthalpies of Dissociation (ΔH) of the Dimers of 2 (3) in Benzene Solution[a]

dimer	ΔH, kcal/mol
2a–2a (3a)	20.4 ± 0.5 (20.7 ± 0.8)[b]
2b–2b (3b)	20.8 ± 0.6
2c–2c (3c)	20.9 ± 0.3 (21.1 ± 1.4)[b]
2d–2d (3d)	(20.2 ± 1.0)[b]
2h–2h (3h)	20.3 ± 0.2
2j–2j (3j)	20.8 ± 0.6
2m–2m (3m)	20.5 ± 0.7

[a] Unless otherwise noted, ΔH values were calculated by method a (see text). [b] The values in parentheses were calculated by method b (see text).

from the table, the values obtained by method a are in good agreement with those from method b.

Discussion

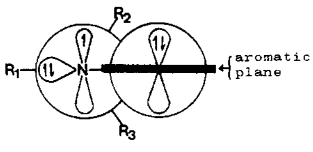
ESR Parameters. The a_N values for 2 exist in the relatively narrow range of 11.6–12.26 G and show no temperature dependence in the range of 24 to 31 °C. Furthermore, they were scarecely affected by the polarity of the solvents. The magnitudes of the a_N values for 2 are obviously different from those for the corresponding nitroxide radicals.[16] For example, the a_N values for arylthio *tert*-butyl nitroxide radicals lie in the range of 16.75–18.18 G. Thus, we can safely rule out the possibility that the radicals examined in the present work are not the corresponding nitroxide radicals.

Although the a_N values for 2 are not significantly changed by the substituents, they are somewhat increased by electron-withdrawing substituents and reduced by electron-donating ones (but **2n** is not the case as described below), as found in Table I. These increases and reductions in a_N can easily explained in terms of the inductive effects of substituents. That is, electron-withdrawing substituents will increase a_N values by stabilizing canonical structure A relative to canonical structure B and elec-

$$\underset{\text{A}}{\text{R}-\dot{\text{N}}-\ddot{\text{S}}-\text{Ar}} \longleftrightarrow \underset{\text{B}}{\text{R}-\ddot{\text{N}}^{-}-\dot{\text{S}}^{+}-\text{Ar}}$$

tron-donating substituents will reduce a_N values by stabilizing B relative to A. The increased $a_{^{33}S}$ value for **2b**, compared with that for **2k**, can also be explained in terms of the inductive effects of substituents. However, electron-withdrawing substituents will reduce $a_{^{33}S}$ values and electron-donating ones will increase them.

The polysubstituted *N*-thioaminyl radical, **2n**, shows interesting differences in its ESR parameters. The X-ray crystallographic analysis of the *N*-[(4-nitrophenyl)thio]-2,4,6-tri-*tert*-butylphenylaminyl radical crystal[4] and the ab initio molecular orbital calculations on HṄSH radical[17] both strongly suggested that *N*-thioaminyl radicals usually adopted a planar conformation (see, 4) in which the nitrogen and sulfur atoms and the benzene ring were in the same plane. However, radical **2n** seems not to adopt such a planar conformation. In spite of the introduction of electron-donating methyl groups, the a_N value for **2n** is increased by 0.48 G, compared with that for **2a**. Furthermore, the $a_{^{33}S}$ value for **2n** which is 0.6 G larger than that for **2b** can not be fully rationalized only by the inductive effect due to the methyl groups because the increase in $a_{^{33}S}$ found on going from **2k** to **2b** is only 0.35 G. Therefore, we wish to explain the unusual increases in a_N and $a_{^{33}S}$ found for **2n** in terms of a twisted conformation (see, 5) in which the benzene ring does not lie in the nodal plane of the sulfur 3p$_z$ (and nitrogen 2p$_z$) orbital.[18] In this conformation there will be poor overlap between the sulfur 3p$_z$ orbital and the benzene π-system. As a result, in **2n** the unpaired electron will not be so much delocalized over the benzene ring as in the cases of the other 2, which adopt a planar conformation, and this situation will increase the a_N and $a_{^{33}S}$ values for **2n**. In addition, the higher *g* value found for **2n** seems also to suggest the twisted conformation.



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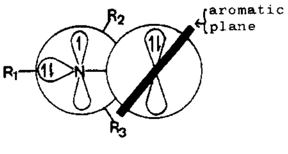

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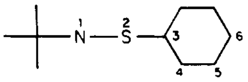
Table III. Observed and Calculated Spin Densities in 2a



no.	exptl hfs, G	exptl spin density[a]	calcd spin density	
			HMO	McLachlan[b]
1	11.78	0.535	0.554	0.754
2	6.1[c]	0.27	0.325	0.234
3			0.000	−0.025
4	1.0	0.037	0.040	0.023
5			0.000	−0.013
6	1.0	0.037	0.040	0.017

[a] Obtained by the simple McConnell equation ($a_x = Q_x\rho_x^{\pi}$), where $Q_H = -27$, $Q_N = 22$, $Q_{^{33}S} = 23$ G. [b] $\lambda = 0.7$. [c] The value for **2b** is quoted. [d] Adoption of the value of $Q_{^{33}S} = 33$ G yields $\rho_s^{\pi} = 0.19$.[21]

Spin Densities in 2. As suggested by the large a_N and $a_{^{33}S}$ values for 2, the unpaired electron seems to reside mainly on the nitrogen and sulfur. To discuss this point in more detail, we performed the calculations of the spin densities in **2a** by the standard Hückel molecular orbital (HMO) method and the McLachlan perturbation treatment,[20] assuming the radical to be planar. The parameters used in this work are as follows: $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, which are the same as those used in the calculations of the other *N*-thioaminyl radicals reported.[17] The results of the calculations are listed in Table III. As found in the table, the results from the HMO method are in good agreement with experiment and predict that the spin densities on the nitrogen and sulfur are ~50 and ~30%, respectively. The disagreement between the results from the McLachlan perturbation treatment and experiment may be attributable to the presence of heteroatoms bearing a high spin density.

For the radicals (anion, cation, and neutral) containing sulfur the spin density on sulfur can be estimated directly from the $a_{^{33}S}$ value, if hyperfine splittings (hfs's) due to ^{33}S can be detected in their ESR spectra. Sullivan showed, in the study on nonplanar sulfide radical cations, that the simple McConnell type equation, $a_{^{33}S} = Q_{^{33}S}\rho_s^{\pi}$, where $Q_{^{33}S}$ is 33 G, yielded a good agreement with experiment.[21] This relationship was further supported by the study on planar sulfide radical cations.[22] However, we showed in a pre-

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[16] Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1983**, *105*, 1937.

[17] Miura, Y.; Asada, H.; Kinoshita, M.; Ohta, K. *J. Phys. Chem.* **1983**, *87*, 3450.

[18] A similar conformation was also suggested for some polysubstituted *N*-(arylthio)arylaminyl radicals on the basis of their ESR parameters.[19]

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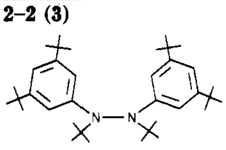
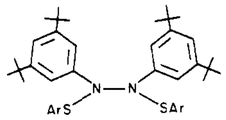
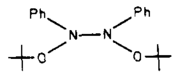
Table IV. Comparison of the Enthalpies of Dissociation (ΔH) of the Dimers of 2 (3) with Those of the Structurally Related Dimers

dimer	ΔH, kcal/mol	solvent	ref
2–2 (3)	20.2–21.1	benzene	this work
 **6**	31.2	methylcyclohexane	23
 **7**	13.3–13.8	benzene	3
 **8**	12.5	toluene	*a*

[a] Kaba, R. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7375.

vious paper[17] that the value of Q_{33_S} = 33 G is not necessarily common and the value of Q_{33_S} = 23 G was valid for *N*-thioaminyl radicals. As found in Table III, when Q_{33_S} = 23 G is employed a better agreement with experiment is given for 2 as well as for the other *N*-thioaminyl radicals reported.[17]

Enthalpies of Dissociation of Dimers. Since relatively few reports on the enthalpies of dissociation (ΔH) for aminyl radicals have appeared in the literature, it is of considerable interest to evaluate the ΔH values for 3.

As found in Table II, the ΔH values (20.2–21.1 kcal/mol) for the dimers are relatively low. As strongly suggested by both the electronic structures of 2 and the analogy to the previously isolated dimers 7,[3] the dimers of 2 are quite probably of the hydrazine type. In Table IV, the ΔH values are compared with those for some hydrazine type dimers which were reported to dissociate into the aminyl radicals in solution. As found in the table, the ΔH values for 3 lie between those for 6 and 7. In particular we were interested in the result that the ΔH values for 3 are 11.5 kcal/mol lower than that for 6.[23] We believe such low ΔH values for 3 result from the structural features in the dimers and radicals which weaken the N–N bond. Since the dipolar repulsion between the nitrogens in the dimers seems to be more enhanced by the presence of the adjacent divalent sulfurs which are an electron-donating group, the dimers seem to be more destabilized. In addition, the dimers seem to be further destabilized by the steric interaction between the two *tert*-butyl groups attached to the nitrogens, but this effect is probably less important in destabilizing the dimers.[23,24] Furthermore, it is easily assumed that radicals 2 are stabilized to a great extent by the conjugative electron delocalization from the nitrogen to the phenylthiyl group, as shown by the canonical structures A and B. As a result, the weak N–N bond of the dimers can be reasonably interpreted in terms of the presence of divalent sulfurs stabilizing the radicals and destabilizing the dimers. On the other hand, in the case of 6, the corresponding radical from 6 ought to be stabilized, probably to a similar or greater extent, by the conjugative electron delocalization from the nitrogen to the benzene ring. Similarly, dimer 6 seems to be stabilized to some extent since the dipolar repulsion between the nitrogens is probably reduced by the presence of the benzene rings removing the lone pairs of electrons on the nitrogens. Therefore, the weaker N–N bonds of 3, compared with that of 6, can be explained by the destabilized structure of 3.

Experimental Section

Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. Elemental combustion analyses were performed with a Yanagimoto MT-2 CHN corder. Proton nuclear magnetic resonance (NMR) spectra were recorded on a JEOR JNM PS-100 spectrometer. Chemical shifts (δ) are expressed in ppm relative to internal tetramethylsilane. Ultraviolet (UV) spectra were taken with a Hitachi ESP-3T spectrophotometer.

Materials. All amines were commercially available and used without further purification. 3-Chloro-,[25] 3,5-dichloro-,[25] and 2,4,6-trimethylbenzenethiols[26] were obtained according to the previously reported methods. Benzene-2,3,4,5,6-d_5-thiol was prepared from benzene-d_6 via chlorosulfonation of the benzene by chlorosulfonic acid and subsequent reduction with Zn in H_2SO_4 aqueous solution (bp 62–63 °C (19 torr)). The deuterium content of the benzenethiol thus obtained was 83% from the integrated signal ratio of aromatic protons to SH proton in the NMR spectrum. Other benzenethiols were commercially obtained and used without further purification. Chlorination of the other benzenethiols except 2,4,6-trimethylbenzenethiol was performed by treating them with chlorine in CH_2Cl_2 or $CHCl_3$ at room temperature.[26] Unsubstituted (81–82 °C (11 torr)), 4-methyl- (102–104 °C (11 torr)), and deuteriated benzenesulfenyl chlorides (95–102 °C (17 torr)) were purified by distillation, while other sulfenyl chlorides were used in the following step without further purification. Chlorination of 2,4,6-trimethylbenzenethiol was performed by treating it with 1 equiv of sulfuryl chloride in $CHCl_3$.[27]

General Procedure for Preparation of *N,N*-Bis(arylthio)alkylamines (1). To a stirred solution of 8.9–9.9 mmol of alkylamine and 3.6 g (36 mmol) of triethylamine in 200 mL of dry diethyl ether (ether) was added dropwise at ca. 5 °C a solution of 26.7–29.7 mmol (3 equiv based on the alkylamine) of a benzenesulfenyl chloride in 50 mL of dry ether. The reaction mixture was then stirred for 2 h at the same temperature and for 12 h at room temperature. After filtration of the mixture, the filtrate was concentrated under reduced pressure to leave a viscous oil or solid mass. In the cases of 1l and 1m the solid mass was recrystallized from hexane to afford colorless crystals of 1l or 1m containing small amounts of bis(*p*-bromophenyl) disulfide, which were further recrystallized from ethanol. In the other cases the concentrate (oil or solid mass) was chromatographed on alumina (Merck, art 1097, column size 4 × 40 cm) with hexane as eluant to give a mixture of 1 and diaryl disulfide. The mixture was again chromatographed similarly to afford almost pure 1 which was recrystallized from the appropriate solvent.

***N,N*-Bis(phenylthio)-*tert*-butylamine (1a):** colorless needles (methanol); mp 70–71 °C; yield 86%; UV (hexane) λ_{max} 248 nm (ϵ 17 900); NMR (CCl_4) δ 1.32 (s, *t*-Bu, 9 H) and 7.03–7.32 (m, aromatic, 10 H). Anal. Calcd for $C_{16}H_{19}NS_2$: C, 66.39; H, 6.62; N, 4.84. Found: C, 65.99; H, 6.58; N, 4.57.

***N,N*-Bis(phenyl-d_5-thio)-*tert*-butylamine (1b):** colorless needles (methanol); mp 70–71 °C; yield 61%; UV (hexane) λ_{max} 248 nm (ϵ 18 200); NMR (CCl_4) δ 1.31 (s, *t*-Bu, 9 H). Anal. Calcd for $C_{16}H_9D_{10}NS_2$: C, 64.16; H, 6.39; N, 4.68. Found: C, 64.51; H, 6.72; N, 4.49.

***N,N*-Bis(phenylthio)-1-adamantanamine (1c):** colorless prisms (methanol); mp 162–163 °C; yield 22%; UV (hexane) λ_{max} 249 nm (ϵ 19 100); NMR (CCl_4) δ 1.56–2.06 (m, adamantyl, 15 H) and 7.03–7.31 (m, aromatic, 10 H). Anal. Calcd for $C_{22}H_{25}NS_2$: C, 71.89; H, 6.86; N, 3.81. Found: C, 72.28; H, 6.88; N, 3.58.

***N,N*-Bis(4-tolylthio)-*tert*-butylamine (1d):** colorless prisms (methanol); mp 63–64 °C; yield 83%; UV (hexane) λ_{max} 249 nm (ϵ 19 500); NMR (CCl_4) δ 1.24 (s, *t*-Bu, 9 H), 2.31 (s, Me, 6 H),

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and 7.00–7.31 (m, aromatic, 8 H). Anal. Calcd for $C_{18}H_{23}NS_2$: C, 68.09; H, 7.30; N, 4.41. Found: C, 68.44; H, 7.18; N, 4.17.

***N*,*N*-Bis[(4-chlorophenyl)thio]-*tert*-butylamine (1e):** colorless prisms (methanol); mp 78–79 °C; UV (hexane) λ_{max} 255 (ϵ 21800) and 231 nm (sh, 16000); NMR (CCl_4) δ 1.30 (s, *t*-Bu, 9 H) and 7.27 (s, aromatic, 8 H). Anal. Calcd for $C_{16}H_{17}Cl_2NS_2$: C, 53.63; H, 4.78; N, 3.91. Found: C, 53.33; H, 4.88; N, 3.97.

***N*,*N*-Bis[(4-chlorophenyl)thio]isopropylamine (1f):** colorless needles (methanol); mp 80.5–81.5 °C; yield 47% UV (hexane) λ_{max} 252 nm (ϵ 21800); NMR (CCl_4) δ 1.16 (d, *J* = 5.9 Hz, Me, 6 H), 3.65 (sept, *J* = 5.9 Hz, Me_2CH, 1 H), and 7.29 (s, aromatic, 8 H). Anal. Calcd for $C_{15}H_{15}Cl_2NS_2$: C, 52.32; H, 4.39; N, 4.07. Found: C, 51.93; H, 4.40; N, 3.95.

***N*,*N*-Bis[(4-chlorophenyl)thio]cyclohexylamine (1g):** colorless needles (ethanol); mp 75–76 °C; yield 72%; UV (hexane) λ_{max} 252 nm (ϵ 22000); NMR (CCl_4) δ 1.06–2.05 [br, $(CH_2)_5$, 10 H], 3.18 (br s, CHN, 1 H), and 7.36 (s, aromatic, 8 H). Anal. Calcd for $C_{18}H_{19}Cl_2NS_2$: C, 56.24; H, 4.98; N, 3.64. Found: C, 56.18; H, 5.04; N, 3.68.

***N*,*N*-Bis[(4-chlorophenyl)thio]-1-adamantanamine (1h):** colorless needles (ethanol); mp 128–129 °C; yield 41%; UV (hexane) λ_{max} 256 (ϵ 23800) and 233 nm (16500); NMR (CCl_4) δ 1.56–2.08 (m, adamantyl, 15 H) and 7.27 (s, aromatic, 8 H). Anal. Calcd for $C_{22}H_{23}Cl_2NS_2$: C, 60.54; H, 5.31; N, 3.21. Found: C, 60.22; H, 5.35; N, 3.22.

***N*,*N*-Bis[(3-chlorophenyl)thio]-*tert*-butylamine (1i):** viscous oil (not distilled, TLC almost one spot); yield 50%; NMR (CCl_4) δ 1.34 (s, *t*-Bu, 9 H) and 7.14–7.29 (m, aromatic, 8 H). The elemental analyses were unsatisfactory (C, 51.90; H, 4.74; N, 3.11).

***N*,*N*-Bis[(3-chlorophenyl)thio]-1-adamantanamine (1j):** colorless prisms (methanol); mp 114–116 °C; yield 25%; UV (hexane) λ_{max} 253 (ϵ 22700) and 229 nm (sh, 14900); NMR (CCl_4) δ 1.59–2.10 (m, adamantyl, 15 H) and 7.11–7.25 (m, aromatic, 8 H). Anal. Calcd for $C_{22}H_{23}Cl_2NS_2$: C, 60.54; H, 5.31; N, 3.21. Found: C, 60.17; H, 5.19; N, 3.24.

***N*,*N*-Bis[(3,5-dichlorophenyl)thio]-*tert*-butylamine (1k):** colorless prisms (ethanol); mp 117.5–118.5 °C; yield 6.2%; UV (hexane) λ_{max} 256 nm (ϵ 18400); NMR (CCl_4) δ 1.37 (s, *t*-Bu, 9 H) and 7.15 (s, aromatic, 6 H). Anal. Calcd for $C_{16}H_{15}Cl_4NS_2$: C, 44.98; H, 3.54; N, 3.28. Found: C, 44.82; H, 3.52; N, 3.14.

***N*,*N*-Bis[(4-bromophenyl)thio]-*tert*-butylamine (1l):** colorless prisms (ethanol); mp 123.5–125.5 °C; yield 66%; UV (hexane) λ_{max} 256 nm (ϵ 25200); NMR (CCl_4) δ 1.29 (s, *t*-Bu, 9 H) and 7.21 and 7.44 (d, *J* = 9.0 Hz, aromatic, 8 H). Anal. Calcd for $C_{16}H_{17}Br_2NS_2$: C, 42.97; H, 3.83; N, 3.13. Found: C, 43.30; H, 3.78; N, 2.98.

***N*,*N*-Bis[(4-bromophenyl)thio]-1-adamantanamine (1m):** colorless prisms (ethanol); mp 153–155 °C; yield 40%; UV (hexane) λ_{max} 257 nm (ϵ 25600); NMR (CCl_4) δ 1.56–2.07 (m, adamantyl, 15 H) and 7.18 and 7.41 (d, *J* = 9.0 Hz, 8 H). Anal. Calcd for $C_{22}H_{23}Br_2NS_2$: C, 50.29; H, 4.41; N, 2.67. Found: C, 49.92; H, 4.31; N, 2.49.

***N*,*N*-Bis[(2,4,6-trimethylphenyl)thio]-*tert*-butylamine (1n):** colorless prisms (methanol); mp 100–101.5 °C; yield 15%; UV (hexane) λ_{max} 249 (sh, ϵ 19500) and 211 nm; NMR (CCl_4) δ 1.17 (s, *t*-Bu, 9 H), 2.19 (s, *p*-Me, 6 H), 2.42 (s, *o*-Me, 12 H), and 6.71 (s, aromatic, 4 H). Anal. Calcd for $C_{22}H_{31}NS_2$: C, 70.72; H, 8.36; N, 3.75. Found: C, 71.00; H, 8.67; N, 3.77.

ESR Measurements. *N*,*N*-Bis(arylthio)alkylamine (10–30 mg) and 0.20–0.40 mL of solvent were placed in an ESR cell, the mixture was degassed by three freeze–pump–thaw cycles, and the cell was sealed off from the vacuum system. The cell was then set in the cavity of an ESR spectrometer and irradiated with a high-pressure mercury lamp (JEOL JES-UV-1, 100 W). ESR spectra were recorded during the irradiation or after interruption of the irradiation 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 constants and *g* values were determined by comparison with those for Fremy's salt in K_2CO_3 aqueous solution (a_N 13.09 G, *g* 2.0057).

Determination of the Enthalpies of Dissociation for Dimers 3. Samples were prepared as described above. The samples were placed in the cavity of an ESR spectrometer and the peak-to-peak line width (w) and peak-to-peak amplitude (h) of the ESR signal were measured at five different temperatures between 6 and 35 °C. In the cases of **2a**, **2c**, and **2d** the relative radical concentration was also estimated by the area (s) under the absorption curve of the integrated ESR spectrum. The integration was performed with a JEOL JES-ID-2 integrator. The enthalpies of dissociation of **3** were obtained from the least-squares slopes of plots of $\ln w^2hT$ (or $\ln sT$) vs. $1/T$.[13,14] The measurements were repeated at least four times for each radical and averaged. The errors reported in Table II refer to the maximum deviation from the average value.

Registry No. **1a**, 90584-40-0; **1b**, 90584-41-1; **1c**, 90584-42-2; **1d**, 90584-43-3; **1e**, 90584-44-4; **1f**, 90584-45-5; **1g**, 90584-46-6; **1h**, 90584-47-7; **1i**, 90584-48-8; **1j**, 90584-49-9; **1k**, 90584-50-2; **1l**, 90584-51-3; **1m**, 90584-52-4; **1n**, 90584-53-5; **2a**, 64178-06-9; **2b**, 90584-54-6; **2c**, 90584-55-7; **2d**, 90584-56-8; **2e**, 64178-07-0; **2f**, 90584-57-9; **2g**, 90584-58-0; **2h**, 90584-59-1; **2i**, 90584-60-4; **2j**, 90584-61-5; **2k**, 90584-62-6; **2l**, 64209-54-7; **2m**, 90584-63-7; **2n**, 90584-64-8.

Photochemical Aromatic Cyanomethylation: Aromatic Substitution by Way of Radical Cations

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Photolysis at 254 nm of chloroacetonitrile in the presence of aromatic hydrocarbons led to ring cyanomethylation. In addition radical coupling products were found, especially with toluene where 3-phenylpropionitrile, succinonitrile, and bibenzyl accompanied the tolylacetonitriles. These same byproducts were obtained from toluene and chloroacetonitrile upon thermolysis with peroxide initiators, but no nuclear cyanomethylation was observed. The mechanism for aromatic cyanomethylation involves initial excitation of the aromatic hydrocarbons, followed by an electron transfer (probably by way of an exiplex) to chloroacetonitrile, which was found to quench aromatic fluorescence at high rates. Direct spectral evidence for the resulting radical cation with *p*-dimethoxybenzene was obtained by using laser flash spectroscopy. Loss of a chloride ion from the resulting radical anion produces a cyanomethyl radical in close proximity to an aromatic radical cation. Coupling leads to the aromatic substitution product whereas radicals escaping from the cage account for the observed byproducts.

Aromatic photoalkylations have been accomplished upon photolysis of appropriate alkyl halides with aromatic hydrocarbons (eq 1). Most of these have been alkyl halides with electron-withdrawing substituents attached (eq 1, R

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