

# N,N'-Bis(arylthio)arenecarboximidamidyl Radicals. An Electron Spin Resonance Spectroscopic Study of a New Class of Persistent Nitrogen-Centered Free Radicals<sup>1</sup>

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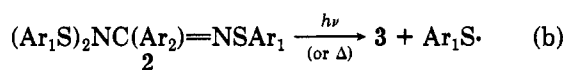
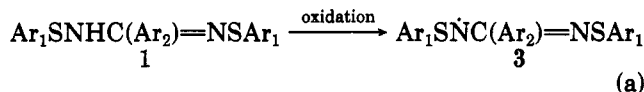
*N,N'*-Bis(arylthio)arenecarboximidamidyl radicals (**3**), ArSNC(Ar')=NSAr, have been studied by electron spin resonance (ESR) spectroscopy. Radicals **3** have been generated by oxidation of ArSNHC(Ar')=NSAr with PbO<sub>2</sub> or Ag<sub>2</sub>O and by photolysis of (ArS)<sub>2</sub>NC(Ar')=NSAr, and their electronic structures are discussed on the basis of their ESR parameters ( $a_N$ ,  $a_H$ ,  $a_{33S}$ , and  $g$ ). The radicals are extremely persistent in solution, even in the presence of oxygen, and exist in equilibrium with the corresponding hydrazine-type dimers which can be isolated as dark green or purplish brown powdery crystals. The equilibrium constants ( $K$ ), enthalpies of dissociation ( $\Delta H^\circ$ ), and entropies of dissociation ( $\Delta S^\circ$ ) for the dimers are ( $4.6 \times 10^{-4}$ )–( $5.3 \times 10^{-4}$ ) M ( $K$ ), 5.9–6.5 kcal/mol ( $\Delta H^\circ$ ), and 4.7–6.7 eu ( $\Delta S^\circ$ ) (in benzene and in toluene), respectively. The facile N–N bond homolysis is discussed in terms of the structures of the radicals and dimers.

Radical persistence is a function of electronic stabilization and steric protection. Thioaminy radicals (RNSR') are significantly stabilized by the conjugative electron delocalization from nitrogen to sulfur.<sup>2</sup> Therefore, when the reaction sites in the radicals are effectively protected by bulky groups, the protected thioaminy radicals are expected to become remarkably long-lived. In fact, some protected thioaminy radicals have been isolated as the hydrazine-type dimers or the radical crystals.<sup>3,4</sup>

In the continued electron spin resonance (ESR) studies of thioaminy radicals, we have found that *N,N'*-bis(arylthio)arenecarboximidamidyl radicals (**3**), a new class of nitrogen-centered free radicals, persist in solution and can be isolated as hydrazine-type dimers.<sup>5</sup> As can be seen from the structures of **3**, there are no intended protecting groups in them. Accordingly, the radical persistence seems to result principally from the resonance stabilization. We report herein the ESR spectra of **3** and isolation of the dimers and their chemical and physical properties.

## Results

**Generation of Radicals.** Radicals **3** were generated in benzene and in hexane by two methods: (a) oxidation



of *N,N'*-bis(arylthio)arenecarboximidamides (**1**) with PbO<sub>2</sub> or Ag<sub>2</sub>O and (b) photolysis of *N,N,N'*-tris(arylthio)arenecarboximidamides (**2**) with a high-pressure mercury lamp. The ESR parameters for **3** are summarized in Table I and a representative ESR spectrum is illustrated in Figure 1.

Upon addition of the oxidizing agents, solutions of **1** turned immediately green, brown, or blue. This charac-

teristic coloration was also found on photolysis of solutions of **2**. Furthermore, when solutions of **2** were heated to ~50 °C, the same color also appeared immediately. In any case, the colored solutions yielded an intense ESR signal due to **3** which was constituted of an 1:2:3:2:1 quintet splitting with a relatively large line width ( $\Delta H$  ca. 1.8 G), as found in Figure 1. This splitting pattern can be readily interpreted in terms of the interaction with two magnetically equivalent nitrogens. In addition, in the spectra of **3g** and **3r** each line of the quintet was further split into a septet by the interaction with the six ortho and para protons of the two phenylthio benzene rings (S-benzene rings), though their resolution was quite poor. Furthermore, in the spectra of **3b**, **3s**, and **3t**, which have relatively narrow lines ( $\Delta H$  ca. 1.1 G), satellite lines due to <sup>33</sup>S atoms at natural abundance (0.76%) could be detected at each end of the spectrum, on recording at high gain. The heights of the satellite lines revealed that these are due to two magnetically equivalent <sup>33</sup>S atoms.

For comparison of ESR parameters, we also generated *N,N'*-bis(*tert*-butylthio)arenecarboximidamidyl radicals **4** and **5** (see Table I). Although, in this case, the precursors corresponding to **1** or **2** could not be isolated from the reaction mixtures (brownish green or greenish brown) which were obtained by treating benzenecarboximidamides with 2-methyl-2-propanesulfonyl chloride in the presence of triethylamine, benzene solutions of the concentrated reaction mixtures afforded a strong 1:2:3:2:1 quintet spectrum due to **4** or **5** with a relatively narrow line width ( $\Delta H$  ca. 0.7 G). The benzene solutions, on heating to ~40 °C, immediately turned green. However, on standing, the color faded soon. The ESR spectra of these radicals, on recording at high gain, also showed satellite lines due to <sup>33</sup>S atoms at natural abundance at each end of the spectrum.

**Isolation of Dimers.** Radicals **3** are quite persistent in hydrocarbon solvents such as benzene, hexane, and toluene, even in the presence of oxygen. For instance, although benzene solutions of **3** in the concentrations of  $10^{-3}$  to  $5 \times 10^{-3}$  M were allowed to stand for 5 h at 14 °C exposed to air, the decreases in the radical concentrations were only a few percents. However, the radicals were less persistent at high temperatures (half-lives at 41 °C ~12 h) and in methanol or in acidic solvents they were immediately decomposed.

It was found that radicals **3** exist in equilibrium with a dimer in solution from the temperature dependence of the

(1) ESR studies of nitrogen-centered free radicals **24**. For part 23, see: Miura, Y.; Isogai, M.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* 1985, 58, 751.

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

(4) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M.; Sato, S.; Tamura, C. *J. Org. Chem.* 1982, 47, 2618.

(5) For a preliminary communication of this work, see: Miura, Y.; Kunishi, T.; Kinoshita, M. *Chem. Lett.* 1983, 885.

Table I. ESR Parameters for *N,N'*-Bis(arylthio)arenecarboximidamidyl Radicals<sup>a,b</sup>

Ar <sub>1</sub> SNC(Ar <sub>2</sub> )=NSAr <sub>1</sub>		Ar <sub>1</sub>	Ar <sub>2</sub>	a <sub>N</sub>	a <sub>other</sub> <sup>c</sup>	g	μ <sub>max</sub> (ε) or color <sup>d,e</sup>	method <sup>f</sup>
3a <sup>g</sup>	Ph	Ph	Ph	6.09		2.0074	green	b
3b	C <sub>6</sub> D <sub>5</sub>	Ph	Ph	6.08	3.31 (2 <sup>33</sup> S)	2.0074	green	b
3c	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	Ph	6.03		2.0074	yellowish green	b
3d	4-ClC <sub>6</sub> H <sub>4</sub>	Ph	Ph	6.13		2.0074	463, <sup>h</sup> 366	a
3d				6.12		2.0074		b
3e	4-BrC <sub>6</sub> H <sub>4</sub>	Ph	Ph	6.09		2.0078	465, <sup>h</sup> 344	a
3e				6.07		2.0078		b
3f	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Ph	Ph	6.10		2.0073	472 <sup>h</sup> (3000), 371 (13400)	a
3f				6.10		2.0073		b
3g	3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Ph	Ph	6.26	0.7 (6 H) <sup>i</sup>	2.0070	468, <sup>h</sup> 326	a
3h	4-MeC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	6.03		2.0074	yellowish green	b
3i	4-ClC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	6.11		2.0074	yellowish green	b
3j	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	6.16		2.0073	474 <sup>h</sup> (3000), 385 <sup>h</sup> (11 000), 357	a
3j				6.20		2.0073		b
3k	4-ClC <sub>6</sub> H <sub>4</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	6.11		2.0074	yellowish brown	b
3l	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	6.16		2.0072	457, 385, <sup>h</sup> 358	a
3l				6.20		2.0072		b
3m	Ph	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.00		2.0074	yellowish green	b
3n	4-MeC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	5.96		2.0075	yellowish green	b
3o	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.06		2.0075	yellowish green	b
3p	3-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.15		2.0072	465, <sup>h</sup> 337	a
3q	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.10		2.0073	475, <sup>h</sup> 373	a
3r	3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.16	0.7 (6 H) <sup>i</sup>	2.0070	467, <sup>h</sup> 350	a
3s	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.33	3.4 (2 <sup>33</sup> S)	2.0083	greenish blue	b
3t	2,3,5,6-Me <sub>4</sub> C <sub>6</sub> H	4-ClC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	6.46	3.4 (2 <sup>33</sup> S)	2.0084	greenish blue	b
3u	Ph	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	5.91		2.0077	610, 348	a
4		<i>t</i> -BuSNC(Ph)=NSBu- <i>t</i>		6.48	3.50 (2 <sup>33</sup> S)	2.0086	green	
5		<i>t</i> -BuSNC(4-ClC <sub>6</sub> H <sub>4</sub> )=NSBu- <i>t</i>		6.48	3.46 (2 <sup>33</sup> S)	2.0087	green	

<sup>a</sup>Solvent benzene, temperature 16–20 °C. <sup>b</sup>Hyperfine splitting constants are given in gauss. <sup>c</sup>Numbers in parentheses refer to the number of equivalent nuclei. <sup>d</sup>λ<sub>max</sub> or color of the radical solution; solvent benzene. <sup>e</sup>λ<sub>max</sub> are given in nm. <sup>f</sup>Method of generation of radicals (see text). <sup>g</sup>The a<sub>N</sub> values for 3a in hexane are almost constant (6.08–6.13 G) in the temperature range of –62 to 22 °C. <sup>h</sup>Shoulder. <sup>i</sup>Magnetically equivalent four ortho and two para protons in the two S-benzene rings.

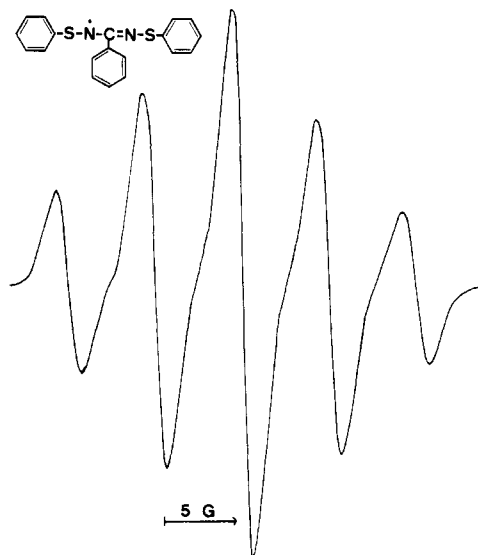
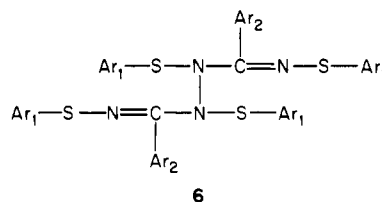


Figure 1. ESR spectrum of 3a generated by photolysis of a solution of 2a in benzene at 16 °C.

ESR signal intensity. When a hexane or toluene solution of 3 was cooled to –50 °C, the ESR signal became remarkably weak and when the solution was raised to room temperature, the signal intensity immediately reverted to the original level and this cycle was completely reversible. The dimers could be isolated by the following procedure: a benzene solution of 1 was stirred in the presence of PbO<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub>. Then the reaction mixture was filtered and the solvent was removed from the filtrate by freeze-drying to leave a dark green or purplish brown crystalline powder. To this powder was added small amounts of hexane and the resultant undissolved powdery crystals were collected and dried (yield 44–54%). The powdery crystals thus

obtained from 1f, 1j, 1l, and 1q were found to be almost completely pure from TLC inspection. However, in other cases the powdery crystals contained small amounts of 1 and/or red polar byproducts and recrystallization or reprecipitation of the crystals caused further decomposition.

The IR spectra of the powdery crystals exhibited no absorption in the region of 3100–3380 cm<sup>-1</sup> corresponding to the N–H stretching frequency. Also, the elemental analyses of the crystals obtained from 1f, 1j, 1l, and 1q were compatible with the dimer structure 6. Accordingly, the crystals were confirmed to be dimers 6.



The dimers thus obtained contained considerable amounts of 3 as shown by their ESR measurements. For instance, dimer 6j was shown to contain ~32 wt % of 3j by comparison of the area of the integrated ESR signal with that of a benzene solution of 1,3,5-triphenylverdazyl.<sup>6</sup> Since dimers 6 exhibited slow decomposition even on storage at 5 °C, the instrumental and elemental analyses were conducted as soon as possible (usually in 1 day).

The equilibrium constants (*K*) for the dimer ⇌ radical

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

equilibria were measured in both benzene and toluene in the temperature range of 35 to –5 °C, and enthalpies of

Table II. Thermodynamic Parameters for 6 = (2)3 Equilibria

	solvent	equilibrium const. <sup>a,c</sup> M	enthalpy of dissociation, <sup>b,c</sup> kcal/mol	entropy of dissociation, <sup>b,c</sup> eu
6f = 2 3f	benzene	$(5.3 \pm 0.5) \times 10^{-4}$	$5.9 \pm 0.2$	$4.9 \pm 0.7$
6f = 2 3f	toluene	$(5.0 \pm 0.3) \times 10^{-4}$	$5.9 \pm 0.1$	$4.7 \pm 0.6$
6j = 2 3j	benzene	$(5.2 \pm 0.6) \times 10^{-4}$	$6.2 \pm 0.5$	$5.7 \pm 1.4$
6j = 2 3j	toluene	$(4.6 \pm 0.2) \times 10^{-4}$	$6.5 \pm 0.1$	$6.7 \pm 0.8$

<sup>a</sup> At 22 °C. <sup>b</sup> Average of four experiments. <sup>c</sup> Error are standard deviations.

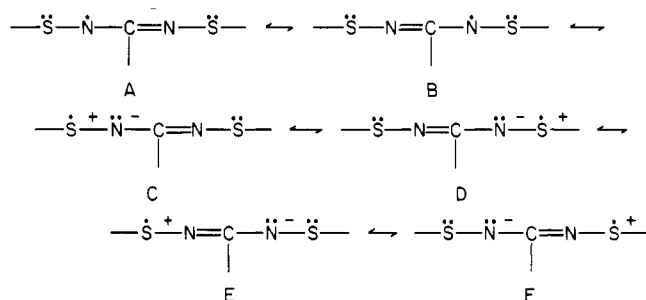
dissociation ( $\Delta H^\circ$ ) and entropies of dissociation ( $\Delta S^\circ$ ) were calculated from the slope of plots of  $\ln K$  vs.  $1/T$ , using the equation  $-RT \ln K = \Delta H^\circ - T\Delta S^\circ$ , where  $R$  is the gas constant and  $T$  is the absolute temperature. The results are summarized in Table II.

### Discussion

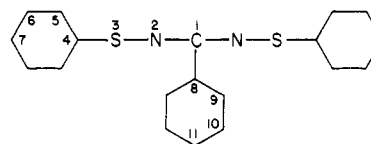
**ESR Parameters.** As can be seen from Figure 1, the two nitrogens of **3** are magnetically equivalent and their hyperfine splitting (hfs) constants (5.91–6.46 G) are only slightly changed by substituents. Similarly, the two sulfurs are also magnetically equivalent and the  $a_{33S}$  values are in the range of 3.31 to 3.4 G. On the other hand, the hfs constants due to the S-benzene ring protons are only 0.7 G and hfs's due to the C-benzene ring protons are not found. These results strongly suggest that in **3** the unpaired electron resides mainly on the two nitrogens and two sulfurs. To confirm this point we calculated the spin density distribution in **3** by the standard Hückel molecular orbital method (HMO) and the McLachlan perturbation treatment,<sup>7</sup> assuming the radicals to be planar.<sup>2</sup> The parameters used in this work are  $\alpha_N = \alpha + 0.6\beta$ ,  $\alpha_S = \alpha + \beta$ ,  $\beta_{CN} = 1.1\beta$ ,  $\beta_{NS} = 0.7\beta$ , and  $\beta_{CS} = 0.7\beta$ . These are the same set of parameters that are used in the previous calculations.<sup>2</sup> The results of the calculations are summarized in Table III.<sup>8</sup>

As can be seen from Table III, the results of the calculations are in good agreement with experiment and predict that the spin is localized mainly on the two nitrogens and two sulfurs and the spin densities on the S- and C-benzene rings are very low or essentially zero.

Accordingly, radicals **3** can be represented by six principal canonical structures A–F and are examples of cap-



totative or merostabilized free radicals.<sup>9</sup> When the S-benzene rings have an electron-withdrawing substituent or the C-benzene ring has an electron-donating substituent, canonical structures A and B will be reinforced. In contrast, when the S-benzene rings have an electron-donating substituent or the C-benzene ring has an electron-withdrawing substituent, canonical structures C–F will be reinforced. These substituent effects are certainly found in

Table III. Observed and Calculated Spin Density Distributions in **3a**

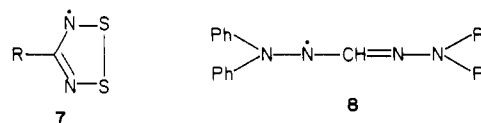
no.	exptl hfs, G	exptl spin density <sup>a</sup>	calcd spin density	
			HMO	McLachlan <sup>b</sup>
1			0.000	-0.054
2 (N)	6.09	0.277	0.277	0.359
3 (S)	3.31 <sup>c</sup>	0.144	0.163	0.148
4			0.000	-0.009
5	0.7 <sup>d</sup>	0.03	0.020	0.018
6			0.000	-0.006
7	0.7 <sup>d</sup>	0.03	0.020	0.016
8			0.000	0.004
9			0.000	-0.008
10			0.000	0.000
11			0.000	0.007

<sup>a</sup> Obtained by the simple McConnell equation  $a_x = Q_x \rho_x^2$ , where  $Q_H = -27$ ,  $Q_N = 22$ , and  $Q_{33S} = 23$  G. <sup>b</sup>  $\lambda = 0.7$ . <sup>c</sup> Value for **3b**. <sup>d</sup> Value for **3g**.

Table I; that is, the slightly higher  $a_N$  values for **3g**, **3j**, **3l**, **3p**, and **3r** and the slightly reduced  $a_N$  values for **3c**, **3h**, **3n**, and **3u** can be accounted for by these substituent effects.

Radicals **3s** and **3t** gave interesting differences in their ESR parameters. In spite of introduction of several methyl groups into the S-benzene rings, the  $a_N$  values are increased. Furthermore, the  $a_{33S}$  and  $g$  values are also unusually increased. Analogous unusual increases in ESR parameters have been found for some polysubstituted (aryltio)aminyl radicals ( $\text{ArSNR}$ ),<sup>10</sup> and these have been accounted for in terms of twisting of the S-benzene rings from the nodal plane of the nitrogen  $2p_z$  orbital. If analogous arguments are applied to the present radicals, the ESR parameters ( $a_N$ ,  $a_{33S}$ , and  $g$ ) for **3s** and **3t** should come close to those for **4** and **5**. As can be seen from Table I, the ESR parameters for **3s** and **3t** are certainly close to those for **4** and **5**. Accordingly, we can conclude that the unusual increases in the  $a_N$ ,  $a_{33S}$ , and  $g$  values found for **3s** and **3t** result from the twisting of the S-benzene rings.

Some structurally related radicals have been found in the literature. Radicals **7** are cyclic analogues<sup>11</sup> and **8** is



a nitrogen analogue.<sup>12</sup> Nitrogen analogue **8** is of considerable interest because it can be isolated as a pure radical substance. Cyclic analogues **7** exhibit considerably lower

(7) McLachlan, A. D. *Mol. Phys.* 1960, 3, 233.

(8) We note that the results from HMO method exhibit a better agreement with experiment. This is probably due to that the conjugated systems of **3** are comprised mainly of heteroatoms.

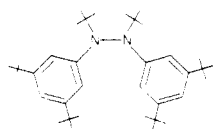
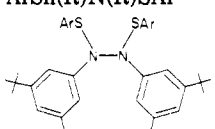
(9) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 917.

(10) (a) Miura, Y.; Katsura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* 1979, 52, 1121. (b) Miura, Y.; Kinoshita, M. *J. Org. Chem.* 1984, 49, 2724.

(11) Markovski, L. N.; Polumbrik, O. M.; Talanov, V. S.; Shermolovich, Y. G. *Tetrahedron Lett.* 1982, 23, 761.

(12) Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* 1973, 12, 455.

Table IV. Comparison of  $\Delta H^\circ$  and  $\Delta S^\circ$  Values for Some Structurally Related Dimers

dimer		$\Delta H^\circ$ , kcal/mol	$\Delta S^\circ$ , eu	solvent	ref
	9	31.2	73.6	methylcyclohexane	a
ArSn(R)N(R)SAr	10	20.2-21.1		benzene	10b
	11	13.3-13.8	29.0-29.2	benzene	3
(CF <sub>3</sub> S) <sub>2</sub> NN(SCF <sub>3</sub> ) <sub>2</sub>	12	7.6	0.7	trichlorofluoro- methane	13
6f and 6j		5.9-6.2	4.9-5.7	benzene	this work
6f and 6j		5.9-6.5	4.7-6.7	toluene	this work

<sup>a</sup> Nelsen, S. F.; Landis, R. T. *J. Am. Chem. Soc.* 1973, 95, 8707.

$\alpha_N$  (4.9 G) and considerably higher  $g$  values (2.0104) than those for 3 and these ESR parameters strongly suggest that in 7 there is a more favored overlap between the nitrogen  $2p_z$  and sulfur  $3p_z$  orbitals. Therefore, radicals 7 persist in solution even in the presence of oxygen. However, they have not yet been isolated as dimers or radical crystals.

**Nature of N-N Bonds.** The remarkably low  $\Delta H^\circ$  values for dimers 6 strongly suggest very weak N-N bonds of 6. These weak N-N bonds appear to result from the structural features in the radicals and the dimers which weaken the N-N bonds.

In Table IV the  $\Delta H^\circ$  and  $\Delta S^\circ$  values for some structurally related hydrazine-type dimers are compared. As can be seen from the table, the corresponding dimers (10<sup>10b</sup> and 11<sup>3</sup>) of thioaminy radicals exhibit relatively low  $\Delta H^\circ$  values. Further lower  $\Delta H^\circ$  values have been reported for dimer 12<sup>13</sup> and for the dimers (6.7-10.0 kcal/mol)<sup>14</sup> of the free radicals formed by reactions of sulfur-nitrogen compounds with olefins.<sup>15</sup> We have interpreted the relatively low  $\Delta H^\circ$  values for 10 and 11 in terms of the presence of divalent sulfurs which will stabilize the corresponding radicals and will destabilize the dimers.<sup>10b,16</sup> That is, in these dimers the dipolar repulsion between the nitrogens will be further enhanced by the presence of the divalent sulfurs releasing the electrons and this enhancement in dipolar repulsion will destabilize the dimers. On the other hand, the radicals will be stabilized by the conjugative electron delocalization with the divalent sulfur.<sup>2</sup> Analogous arguments can be applied to the present radicals and dimers. However, conjugative radical stabilization will be much greater in 3 than in the corresponding radicals from 10 and 11 because of the extended conjugated systems in 3, and this greater stabilization will make the N-N bonds of 6 further weaken.

### Experimental Section

Melting points were taken on a Yanagimoto micro melting point apparatus and uncorrected. Elemental combustion analyses were performed with a Yanagimoto MT-2 CHN corder. Proton nuclear

magnetic resonance (NMR) spectra were recorded with a JEOL JNM PS-100 spectrometer. Chemical shifts,  $\delta$ , are expressed in parts per million relative to internal tetramethylsilane. Infrared (IR) spectra were run on a JASCO A-202 spectrometer, and visible and ultraviolet (UV) spectra were recorded with a Shimadzu UV-240 spectrometer.

4-Chloro-, 4-methyl-, 4-methoxy-, and 4-nitrobenzimidamides and benzenecarboximidamide (benzamide) hydrochloride hydrate were commercially obtained. Unsubstituted and deuterated benzenesulfonyl chlorides, 4-methyl-, 3-chloro-, 4-chloro-, 4-bromo-, 2,4-dichloro-, 3,5-dichloro-, and 2,4,6-trimethylbenzenesulfonyl chlorides, and 2-methyl-2-propanesulfonyl chloride were obtained by the previously reported methods.<sup>2,10b</sup> 2,3,5,6-Tetramethylbenzenethiol was prepared by the reported method<sup>17</sup> and its sulfonyl chloride was obtained by the same procedure as for 2,4,6-trimethylbenzenesulfonyl chloride. Lead dioxide was purified by our previously reported procedure.<sup>3</sup> 4-Methyl-, 4-chloro-, 4-methoxy-, and 4-nitrobenzenecarboximidamide hydrochlorides were prepared by the reported or somewhat modified method.<sup>18,19</sup> Benzenecarboximidamides were liberated from their hydrochlorides as follows: 2 g of a hydrochloride, 50 mL of CHCl<sub>3</sub> (or CH<sub>2</sub>Cl<sub>2</sub>), and 20 mL of 2 N NaOH aqueous solution were put in a separatory funnel and shaken vigorously. The organic layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was evaporated and the crystalline or powdery residue was sublimed: 67 °C (0.1 mmHg) (unsubstituted), 90 °C (0.1 mmHg) (4-methyl), 120 °C (0.1 mmHg) (4-chloro), and 95 °C (0.1 mmHg) (4-methoxy). However, since 4-nitrobenzenecarboximidamide hydrochloride was not soluble in CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>, the hydrochloride was treated with 2 N NaOH aqueous solution without adding the organic solvents. The neutralized carboximidamide was filtered, washed with CHCl<sub>3</sub>, and dried in vacuum. The carboximidamide thus obtained was used in the following step without any further purification.

**General Procedure for Preparation of *N,N'*-Bis(arylthio)arenecarboximidamides (1).** To a stirred solution of 5.1 mmol of a benzenecarboximidamide and 3 mL of triethylamine in 150 mL of dry diethyl ether (ether) was added over a period of 30 min at 0-5 °C 11.2 mmol of a benzenesulfonyl chloride in 30 mL of dry ether. After addition, the reaction mixture was stirred for 2 h at the same temperature and filtered. The filtrate was concentrated under reduced pressure and the residue was column chromatographed on alumina (Merck art 1097, column size 4 × 15 cm) using 1:1 benzene-hexane as eluant to give diaryl

(13) Schlosser, K.; Steenken, S. *J. Am. Chem. Soc.* 1983, 105, 1504.

(14) Fairhurst, S. A.; Sutcliffe, L. H. *J. Chem. Soc., Faraday Trans. 1* 1980, 76, 1490.

(15) It has recently reported that benzo-1,3,2-dithiazol-2-yl radical and its derivatives exhibit no tendency to dimerize even on evaporation of the solvent: Wolmershäuser, G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* 1984, 573.

(16) The weak N-N bond of 12 has been interpreted in terms of sterically and electronically induced destabilization of the N-N bond: see ref 13.

(17) Illuminati, G. *J. Am. Chem. Soc.* 1958, 80, 4945.

(18) Dox, A. W. In "Organic Syntheses"; Wiley: New York, 1941; Collect. Vol. I, p 5.

(19) In the preparation of 4-chloro-, 4-methoxy-, and 4-nitrobenzenecarboximidamides, ethanol, HCl, and NH<sub>3</sub> were used in large excess (usually 2-3 times the literature values) and the reactions with NH<sub>3</sub> were conducted without isolating the intermediate imino ether hydrochlorides. The unreacted benzonitriles were removed by washing the benzenecarboximidamide hydrochlorides with benzene.

disulfide, and subsequent elution with benzene afforded compound 1 containing small amounts of diaryl disulfide, which was recrystallized from the appropriate solvent.<sup>20,21</sup>

**N,N'-Bis[(4-chlorophenyl)thio]benzenecarboximidamide (1d):** colorless needles (from hexane); mp 87–88.5 °C; yield 26%; IR (KBr) 3250 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.74 (s, NH, 1 H), 6.97–7.39 (m, Ar, 13 H). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C, 56.30; H, 3.48; N, 6.91. Found: C, 56.15; H, 3.39; N, 6.59.

**N,N'-Bis[(4-bromophenyl)thio]benzenecarboximidamide (1e):** colorless needles (from hexane); mp 109–110 °C; yield 23%; IR (KBr) 3260 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.73 (s, NH, 1 H), 6.92–7.39 (m, Ar, 13 H). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C, 46.17; H, 2.86; N, 5.67. Found: C, 46.09; H, 2.75; N, 5.47.

**N,N'-Bis[(2,4-dichlorophenyl)thio]benzenecarboximidamide (1f):** colorless prisms (from hexane); mp 122–123 °C; yield 36%; IR (KBr) 3320 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.78 (s, NH, 1 H), 7.02–7.72 (m, Ar, 11 H). Anal. Calcd for C<sub>19</sub>H<sub>12</sub>Cl<sub>4</sub>N<sub>2</sub>S<sub>2</sub>: C, 48.12; H, 2.55; N, 5.91. Found: C, 48.52; H, 2.50; N, 5.86.

**N,N'-Bis[(3,5-dichlorophenyl)thio]benzenecarboximidamide (1g):** colorless needles (from hexane); mp 90.5–91.5 °C; yield 52%; IR (KBr) 3100 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.77 and 5.86 (s, syn and anti NH, 1 H), 6.90–7.38 (m, Ar, 11 H). Anal. Calcd for C<sub>19</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C, 48.12; H, 2.55; N, 5.91. Found: C, 48.26; H, 2.57; N, 6.18.

**N,N'-Bis[(2,4-dichlorophenyl)thio]-4-toluenecarboximidamide (1j):** colorless needles (from hexane); mp 137–139 °C; yield 27%; IR (KBr) 3370 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 2.36 and 2.41 (s, syn and anti CH<sub>3</sub>, 3 H), 5.75 (s, NH, 1 H), 7.04–7.77 (m, Ar, 10 H). Anal. Calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C, 49.19; H, 2.89; N, 5.74. Found: C, 49.34; H, 2.77; N, 5.71.

**N,N'-Bis[(2,4-dichlorophenyl)thio]-4-methoxybenzenecarboximidamide (1i):** colorless needles (from hexane–benzene); mp 129–130 °C; yield 46%; IR (KBr) 3290 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 3.76 and 3.81 (s, syn and anti OCH<sub>3</sub>, 3 H), 5.74 (s, NH, 1 H), 6.09–7.74 (m, Ar, 10 H). Anal. Calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>OS<sub>2</sub>: C, 47.64; H, 2.80; N, 5.56. Found: C, 47.64; H, 2.94; N, 5.52.

**N,N'-Bis[(3-chlorophenyl)thio]-4-chlorobenzenecarboximidamide (1p):** colorless prisms (from hexane–ethanol); mp 101–102 °C; yield 24%; IR (KBr) 3180 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.76 and 5.94 (s, syn and anti NH, 1 H), 6.93–7.41 (m, Ar, 12 H). Anal. Calcd for C<sub>19</sub>H<sub>13</sub>Cl<sub>3</sub>N<sub>2</sub>S<sub>2</sub>: C, 51.89; H, 2.98; N, 6.37. Found: C, 51.64; H, 3.14; N, 6.22.

**N,N'-Bis[(2,4-dichlorophenyl)thio]-4-chlorobenzenecarboximidamide (1q):** colorless prisms (from hexane); mp 118–120 °C; yield 31%; IR (KBr) 3380 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.76 (s, NH, 1 H), 7.10–7.71 (m, Ar, 10 H). Anal. Calcd for C<sub>19</sub>H<sub>11</sub>Cl<sub>5</sub>N<sub>2</sub>S<sub>2</sub>: C, 44.86; H, 2.18; N, 5.51. Found: C, 45.18; H, 2.38; N, 5.43.

**N,N'-Bis[(3,5-dichlorophenyl)thio]-4-chlorobenzenecarboximidamide (1r):** colorless prisms (from hexane); mp 95.5–97.5 °C; yield 26%; IR (KBr) 3310 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.72 and 5.88 (s, syn and anti NH, 1 H), 6.95–7.40 (m, Ar, 10 H). Anal. Calcd for C<sub>19</sub>H<sub>11</sub>Cl<sub>5</sub>N<sub>2</sub>S<sub>2</sub>: C, 44.86; H, 2.18; N, 5.51. Found: C, 45.16; H, 2.50; N, 5.20.

**N,N'-Bis[(phenylthio)-4-nitrobenzenecarboximidamide (1u):** greenish yellow prisms (from hexane); mp 96–99 °C; yield 1.7%; IR (KBr) 3310 cm<sup>-1</sup> (NH); NMR (CCl<sub>4</sub>) δ 5.73 (s, NH, 1 H), 7.01–7.40 (m, S-Ar, 10 H), 7.60 and 8.08 (d, *J* = 9 Hz, C-Ar, 4 H). Anal. Calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C, 59.82; H, 3.96; N, 11.02. Found: C, 60.20; H, 3.95; N, 10.92.

**General Procedure for Preparation of N,N,N'-Tris(arylthio)arene-carboximidamides (2).** To a stirred solution of 5.1 mmol of a benzenecarboximidamide and 3 mL of triethylamine in 150 mL of dry ether was added over a period of 30 min at 0–5 °C a solution of 17.8 mmol of a benzenesulfonyl chloride in 30 mL of dry ether. After addition, the reaction mixture was stirred for 2 h at the same temperature and filtered (the reaction mixture turned light yellowish green or light brown

during the stirring of 2 h). The filtrate was concentrated under reduced pressure and the residue (crystals or oil) was recrystallized from the appropriate solvent.

**N,N,N'-Tris(phenylthio)benzenecarboximidamide (2a):** colorless needles (from hexane); mp 94.5–95.5 °C dec; yield 69%; NMR (CCl<sub>4</sub>) δ 7.31 (br s, Ar). Anal. Calcd for C<sub>25</sub>H<sub>20</sub>N<sub>3</sub>S<sub>3</sub>: C, 67.53; H, 4.53; N, 6.30. Found: C, 67.62; H, 4.62; N, 6.46.

**N,N,N'-Tris[(phenyl-*d*<sub>5</sub>)thio]benzenecarboximidamide (2b):** colorless needles (from hexane); mp 90–91.5 °C dec; yield 50%; NMR (CCl<sub>4</sub>) δ 7.27 (br s, Ar). Anal. Calcd for C<sub>25</sub>H<sub>5</sub>D<sub>15</sub>N<sub>3</sub>S<sub>3</sub>: C, 65.31; H, 4.38; N, 6.09. Found: C, 64.98; H, 4.49; N, 6.24.

**N,N,N'-Tris(4-tolylthio)benzenecarboximidamide (2c):** colorless needles (from hexane); mp 87–89 °C dec; yield 73%; NMR (CCl<sub>4</sub>) δ 2.29 (s, CH<sub>3</sub>, 9 H), 7.05–7.26 (m, Ar, 17 H). Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>3</sub>S<sub>3</sub>: C, 69.10; H, 5.38; N, 5.76. Found: C, 69.54; H, 5.49; N, 5.85.

**N,N,N'-Tris[(4-chlorophenyl)thio]benzenecarboximidamide (2d):** light green needles (from benzene–hexane); mp 111–112 °C dec; yield 65%; NMR (CCl<sub>4</sub>) δ 7.29 (br s, Ar). Anal. Calcd for C<sub>25</sub>H<sub>17</sub>Cl<sub>3</sub>N<sub>3</sub>S<sub>3</sub>: C, 54.80; H, 3.13; N, 5.11. Found: C, 54.98; H, 3.28; N, 5.10.

**N,N,N'-Tris[(4-bromophenyl)thio]benzenecarboximidamide (2e):** light green needles (from benzene–hexane); mp 115–117 °C dec; yield 86%; NMR (CCl<sub>4</sub>) δ 7.27–7.53 (m, Ar). Anal. Calcd for C<sub>25</sub>H<sub>17</sub>Br<sub>3</sub>N<sub>3</sub>S<sub>3</sub>: C, 44.07; H, 2.51; N, 4.11. Found: C, 44.09; H, 2.58; N, 4.18.

**N,N,N'-Tris[(2,4-dichlorophenyl)thio]benzenecarboximidamide (2f):** colorless prisms (from benzene–hexane); mp 141–142.5 °C dec; yield 77%; NMR (CCl<sub>4</sub>) δ 7.16–7.78 (m, Ar). Anal. Calcd for C<sub>25</sub>H<sub>14</sub>Cl<sub>6</sub>N<sub>3</sub>S<sub>3</sub>: C, 46.10; H, 2.17; N, 4.30. Found: C, 46.20; H, 2.05; N, 4.36.

**N,N,N'-Tris(4-tolylthio)-4-toluenecarboximidamide (2h):** colorless needles (from hexane); mp 90–92.5 °C dec; yield 74%; NMR (CCl<sub>4</sub>) δ 2.27 (s, CH<sub>3</sub>, 3 H), 2.30 (s, CH<sub>3</sub>, 9 H), 7.04–7.30 (m, Ar, 16 H). Anal. Calcd for C<sub>29</sub>H<sub>28</sub>N<sub>3</sub>S<sub>3</sub>: C, 69.56; H, 5.64; N, 5.59. Found: C, 69.30; H, 5.52; N, 5.69.

**N,N,N'-Tris[(4-chlorophenyl)thio]-4-toluenecarboximidamide (2i):** colorless needles (from hexane); mp 105–106 °C dec; yield 48%; NMR (CCl<sub>4</sub>) δ 2.39 (s, CH<sub>3</sub>, 3 H), 7.16–7.31 (m, Ar, 16 H). Anal. Calcd for C<sub>26</sub>H<sub>19</sub>Cl<sub>3</sub>N<sub>3</sub>S<sub>3</sub>: C, 55.56; H, 3.41; N, 4.98. Found: C, 55.45; H, 3.44; N, 5.06.

**N,N,N'-Tris[(2,4-dichlorophenyl)thio]-4-toluenecarboximidamide (2j):** colorless prisms (from benzene–hexane); mp 135.5–137 °C dec; yield 61%; NMR (CDCl<sub>3</sub>) δ 2.36 (s, CH<sub>3</sub>, 3 H), 7.17–7.80 (m, Ar, 13 H). Anal. Calcd for C<sub>26</sub>H<sub>16</sub>Cl<sub>6</sub>N<sub>3</sub>S<sub>3</sub>: C, 46.93; H, 2.42; N, 4.21. Found: C, 46.94; H, 2.46; N, 3.95.

**N,N,N'-Tris[(4-chlorophenyl)thio]-4-methoxybenzenecarboximidamide (2k):** colorless needles (from hexane); mp 100–102 °C dec; yield 46%; NMR (CDCl<sub>3</sub>) δ 3.83 (s, OCH<sub>3</sub>, 3 H), 6.92–7.53 (m, Ar, 16 H). Anal. Calcd for C<sub>26</sub>H<sub>19</sub>Cl<sub>3</sub>N<sub>3</sub>OS<sub>3</sub>: C, 54.03; H, 3.31; N, 4.85. Found: C, 53.86; H, 3.34; N, 4.64.

**N,N,N'-Tris[(2,4-dichlorophenyl)thio]-4-methoxybenzenecarboximidamide (2l):** colorless prisms (from benzene–hexane); mp 139–142 °C dec; yield 53%; NMR (CDCl<sub>3</sub>) δ 3.85 (s, OCH<sub>3</sub>, 3 H), 6.91–7.79 (m, Ar, 13 H). Anal. Calcd for C<sub>26</sub>H<sub>16</sub>Cl<sub>6</sub>N<sub>3</sub>OS<sub>3</sub>: C, 45.83; H, 2.37; N, 4.11. Found: C, 46.09; H, 2.46; N, 3.72.

**N,N,N'-Tris(phenylthio)-4-chlorobenzenecarboximidamide (2m):** colorless prisms (from hexane); mp 90–91.5 °C dec; yield 60%; NMR (CCl<sub>4</sub>) δ 7.19–7.31 (m, Ar). Anal. Calcd for C<sub>25</sub>H<sub>19</sub>ClN<sub>3</sub>S<sub>3</sub>: C, 62.68; H, 4.00; N, 5.85. Found: C, 62.44; H, 3.90; N, 5.78.

**N,N,N'-Tris(4-tolylthio)-4-chlorobenzenecarboximidamide (2n):** colorless prisms (from hexane); mp 94–95.5 °C dec; yield 74%; NMR (CCl<sub>4</sub>) δ 2.32 (s, CH<sub>3</sub>, 9 H), 7.05–7.27 (m, Ar, 16 H). Anal. Calcd for C<sub>28</sub>H<sub>25</sub>ClN<sub>3</sub>S<sub>3</sub>: C, 64.53; H, 4.83; N, 5.38. Found: C, 64.30; H, 4.60; N, 5.10.

**N,N,N'-Tris[(4-chlorophenyl)thio]-4-chlorobenzenecarboximidamide (2o):** colorless needles (from benzene–hexane); mp 91–93 °C dec; yield 38%; NMR (CCl<sub>4</sub>) δ 7.10–7.19 (m, Ar). Anal. Calcd for C<sub>25</sub>H<sub>16</sub>Cl<sub>4</sub>N<sub>3</sub>S<sub>3</sub>: C, 51.56; H, 2.77; N, 4.81. Found: C, 51.73; H, 2.83; N, 4.79.

**N,N,N'-Tris[(2,4,6-trimethylphenyl)thio]-4-chlorobenzenecarboximidamide (2s):** colorless prisms (from hexane and then benzene–ethanol); mp 136–137 °C dec; yield 25%; NMR (CCl<sub>4</sub>) δ 2.13, 2.22, 2.25, 2.52 (s, syn- and anti-, and *o*- and *p*-CH<sub>3</sub>,

(20) It was likely that a part of 1 was decomposed during the chromatograph to yield diaryl disulfide as one of the decomposition products. In addition, compounds 2, which coexisted in the reaction mixtures, were also decomposed almost completely during the chromatograph.

(21) In the case of 1u, however, the reaction mixture was chromatographed on silica gel (Wako gel C-200, column size 4 × 15 cm) using 2:1 benzene–hexane as eluant.

27 H), 6.77-6.96 (m, Ar, 10 H). Anal. Calcd for  $C_{34}H_{37}ClN_2S_3$ : C, 67.46; H, 6.16; N, 4.63. Found: C, 67.41; H, 5.81; N, 4.58.

***N,N,N'*-Tris[(2,3,5,6-tetramethylphenyl)thio]-4-chlorobenzenecarboximidamide (2t)**: colorless needles (from hexane and then benzene-ethanol); mp 135-136 °C dec; yield 25%; NMR ( $CCl_4$ )  $\delta$  2.07, 2.19, and 2.49 (s, *syn*- and *anti*-, and *o*- and *m*- $CH_3$ , 36 H) and 6.87-6.96 (m, Ar, 7 H). Anal. Calcd for  $C_{37}H_{43}ClN_2S_3$ : C, 68.65; H, 6.69; N, 4.33. Found: C, 68.36; H, 6.40; N, 4.39.

Although the reaction of unsubstituted or 4-chlorobenzenecarboximidamides with 2-methyl-2-propanesulfonyl chloride was carried out in the same manner as above, no precursors corresponding to 1 or 2 could be isolated from the reaction mixtures. However, the benzene solutions of the concentrates of the reaction mixtures afforded a strong ESR signal due to 4 or 5.

**Isolation of Dimers 6**. Precursor 1 (0.10 g) was completely dissolved in 10 mL of benzene with stirring. To this stirred solution was added 1 g of anhydrous  $K_2CO_3$  and 1-1.5 g of  $PbO_2$ . After the mixture was stirred for 1 min, another 1-1.5 g of  $PbO_2$  was added to the mixture and it was stirred for an additional 1-2 min. After filtration, the benzene was removed by freeze-drying to leave a dark green or purplish brown crystalline powder. To this powder was added 10 mL of hexane and the unresolvable crystalline powder was collected and dried in vacuum [one spot on an alumina TLC (Merck art 1064), eluant benzene-hexane (1/4)]. These dimers thus obtained contained ~32 wt % of radical 3 as shown by ESR measurement.

**Dimer 6f**: dark green prisms; mp 104-106 °C dec; yield 45%; UV-vis (benzene)  $\lambda_{max}$  371, 472 (sh) nm. Anal. Calcd for  $(C_{19}H_{11}Cl_4N_2S_2)_2$ : C, 48.23; H, 2.34; N, 5.92. Found: C, 47.89; H, 2.66; N, 5.80.

**Dimer 6j**: dark green powdery crystals; mp 112-114 °C dec; yield 54%; UV-vis (benzene)  $\lambda_{max}$  357, 385 (sh), 474 (sh) nm. Anal. Calcd for  $(C_{20}H_{13}Cl_4N_2S_2)_2$ : C, 49.30; H, 2.69; N, 5.75. Found: C, 49.43; H, 2.92; N, 5.78.

**Dimer 6l**: dark purplish brown powdery crystals; mp 109.5-111 °C dec; yield 53%; UV-vis (benzene)  $\lambda_{max}$  358, 385 (sh), 457 nm. Anal. Calcd for  $(C_{20}H_{13}Cl_4N_4OS_2)_2$ : C, 47.73; H, 2.60; N, 5.57. Found: C, 47.29; H, 2.67; N, 5.47.

**Dimer 6q**: dark green powdery crystals; mp 120.5-122 °C dec; yield 44%; UV-vis (benzene)  $\lambda_{max}$  373, 475 (sh) nm. Anal. Calcd for  $(C_{19}H_{10}Cl_5N_2S_2)_2$ : C, 44.95; H, 1.99; N, 5.52. Found: C, 45.12; H, 2.26; N, 5.52.

**ESR Measurements**. Radicals 3 were generated in benzene or hexane by the following methods: (a) oxidation of 1 with inorganic oxidizing agents such as  $PbO_2$  and  $Ag_2O$  in the presence of  $K_2CO_3$  and (b) photolysis of 2 with a high-pressure mercury lamp.

ESR spectra were recorded with a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants and *g* values were determined by comparison with those ( $a_N$  13.09, *g* 2.0057) for Fremy's salt in  $K_2CO_3$  aqueous solution.

**Measurements of Equilibrium Constants**. Dimer 6 (5-10 mg) was dissolved in 25 mL of benzene or toluene. Then, 0.40 mL of the solution was placed in an ESR cell and its integrated ESR signal was recorded with the ESR instrument equipped with a JEOL JES-ID-2 integrator. The area under the integrated ESR signal was determined by its weight. Calibration curves were obtained as follows: 0.40 mL of a benzene or toluene solution of 1,3,5-triphenylverdazyl<sup>6</sup> was placed in the same cell as used for the dimer solutions and its integrated ESR signal was recorded with the same instrument settings as above. The calibration curves were drawn with the verdazyl solutions of three different concentrations (0.20-1.00 mM). Equilibrium constants (*K*) were measured at four different temperatures between 6 and 35 °C when benzene was used as solvent and at five different temperatures between -5 and 35 °C when toluene was used as solvent. The temperatures of the ESR cavity were measured with a copper-constantan thermocouple.

**Registry No.** 1d, 95674-83-2; 1e, 95674-84-3; 1f, 95674-85-4; 1g, 95674-86-5; 1j, 95674-87-6; 1i, 95674-88-7; 1p, 95674-89-8; 1q, 95674-90-1; 1r, 95674-91-2; 1u, 95674-92-3; 2a, 95674-93-4; 2b, 95674-94-5; 2c, 95674-95-6; 2d, 95674-96-7; 2e, 95674-97-8; 2f, 95674-98-9; 2h, 95674-99-0; 2i, 95675-00-6; 2j, 95675-01-7; 2k, 95675-02-8; 2l, 95675-03-9; 2m, 95675-04-0; 2n, 95675-05-1; 2o, 95675-06-2; 2s, 95675-07-3; 2t, 95675-08-4; 3a, 86602-13-3; 3b, 86602-14-4; 3c, 86602-15-5; 3d, 86602-16-6; 3e, 86602-17-7; 3f, 86602-18-8; 3g, 86602-19-9; 3h, 95675-09-5; 3i, 95675-10-8; 3j, 95675-11-9; 3k, 95675-12-0; 3l, 95675-13-1; 3m, 95675-14-2; 3n, 95675-15-3; 3o, 95675-16-4; 3p, 95675-17-5; 3q, 95675-18-6; 3r, 95675-19-7; 3s, 95675-20-0; 3t, 95675-21-1; 3u, 95675-22-2; 4, 95675-23-3; 5, 95675-24-4; 6f, 95675-25-5; 6j, 95675-26-6; 6l, 95675-27-7; 6q, 95675-28-8.

## Total Synthesis of Pseudoguaianolides IV: A Stereoselective Approach to Balduilin

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9-Acetoxy-camphor oxime undergoes Beckman fragmentation to provide an intermediate (13) from which bicyclo[5.3.0]decane synthons for balduilin are constructed. The vital C-6  $\beta$ -hydroxy group is introduced in a highly stereoselective step (14  $\rightarrow$  15) with remote asymmetric induction resulting from lithium ion chelation during 2-lithio-1,3-dithiane addition.

The pseudoguaianolides are among the most biogenetically advanced and structurally complex members of the sesquiterpene lactones.<sup>1</sup> The abundance of closely placed functional groups, along with up to seven chiral centers

on the flexible seven-membered ring portion of the trans-fused bicyclo[5.3.0]decane framework have made these compounds attractive synthetic targets.<sup>2</sup> The challenge of total synthesis is additionally enhanced by the interesting biological activity displayed by many pseudo-

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