ESR Studies of Dibenzenesulfenamidyl Radicals[1)]

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Dibenzenesulfenamidyl radicals (**2**) were generated by the oxidation of dibenzenesulfenamides (**1**), and their ESR and visible spectra were measured. The ESR spectra were split into a 1 : 1 : 1 triplet by the interaction with the nitrogen nucleus (a_N=11.26—11.49 G); in some spectra, each of the triplet was further split by the interaction with the ring protons ($a_{o\text{-H}}=a_{p\text{-H}}$=0.48—0.70, $a_{m\text{-H}}$=0.18—0.22 G). The *g*-values lay in the range of 2.0080—2.0083. From the results, it was concluded that the unpaired electron is distributed mainly on the nitrogen and the two sulfur atoms. Kinetic studies of the decay of **2** indicated that **2** decays with second-order kinetics and is not sensitive to the atmospheric oxygen.

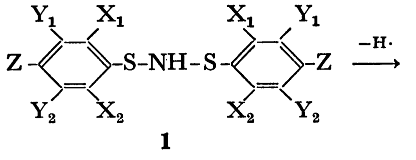
A number of nitrogen-centered free radicals have so far been prepared, and extensive ESR studies for such radicals have been undertaken.[2)] Some of them can be readily isolated as pure crystals: 2,2-diphenyl-1-picrylhydrazyl (DPPH),[3)] 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (1,3,5-triphenylverdazyl),[4)] *etc.*

About fifty years ago, Lecher *et al.* reported that dibenzenesulfenamide (**1a**) in benzene gives a purple solution on treatment with lead dioxide or silver oxide.[5)] They inferred from the coloration that a new class of nitrogen-centered free radicals, dibenzenesulfenamidyl radical (**2a**), had been generated. This radical possesses an interesting structure in which two divalent sulfur atoms are adjacent to the radical center. Barton *et al.* have recently found that tribenzenesulfenamide (**3a**) affords **2a** on photolysis or pyrolysis.[6)] ESR studies on dibenzenesulfenamidyl radicals (**2**), however, have been rare. In this paper, the authors wish to report a detailed ESR investigation of **2**.

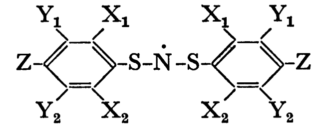
Results and Discussion

Generation of Radicals. Eighteen dibenzenesulfenamides (**1**) were prepared according to a procedure similar to that in the literature.[5)] The compounds **1** in benzene all afforded immediately a purple solution on treatment with lead dioxide and potassium carbonate, and the solution showed a strong ESR signal. The ESR parameters for the radicals are listed in the table. The radicals are also generated by the photolysis of **1**, with or without the assistance of di-*t*-butyl peroxide. In general, nitrogen-centered free radicals are easily converted to the corresponding nitroxide radicals. However, even if the present radicals were treated under exposure to the atmosphere, the corresponding nitroxide radicals were not detected. The compounds **1** were not oxidized to **2** by the atmospheric oxygen, but they were subject to photolysis under exposure to the sunlight to give **2**.

Visible Spectra of Radicals. It is important to prove that the radicals **2** are responsible for the purple colors. For example, a visible spectrum of **2a** in benzene shows a λ_{max} at 538 nm, which is responsible for the purple color. The absorbance at this point was plotted against the intensity of the ESR signal (Fig. 1). The good linearity of the plot indicates that the purple color is attributable to the radical. The absorption maxima of **2** are summarized in the table.



1



2

a: $X_1=X_2=Y_1=Y_2=Z=H$
b: $X_1=X_2=Y_1=Y_2=H,\ Z=CH_3$
c: $X_1=X_2=Y_1=Y_2=H,\ Z=C(CH_3)_3$
d: $X_1=X_2=Y_1=Y_2=H,\ Z=NO_2$
e: $X_1=X_2=Y_1=Y_2=H,\ Z=F$
f: $X_1=X_2=Y_1=Y_2=H,\ Z=Cl$
g: $X_1=X_2=Y_1=Y_2=H,\ Z=Br$
h: $X_1=X_2=Y_1=Z=H,\ Y_2=Cl$
i: $X_1=X_2=Y_1=Z=H,\ Y_2=Br$
j: $X_1=Y_1=Y_2=Z=H,\ X_2=CH_3$
k: $X_1=Y_1=Y_2=Z=H,\ X_2=Cl$
l: $X_1=Y_1=Y_2=Z=H,\ X_2=Br$
m: $X_1=Y_1=Y_2=H,\ X_2=Z=CH_3$
n: $X_1=Y_1=Y_2=H,\ X_2=CH_3,\ Z=Cl$
o: $X_1=Y_1=Y_2=H,\ X_2=Z=Cl$
p: $X_1=Y_2=Z=H,\ X_2=Y_2=Cl$
q: $X_1=Y_1=Z=H,\ X_2=Y_1=Cl$
r: $X_1=X_2=Z=H,\ Y_1=Y_2=Cl$

ESR Spectra of Radicals. The ESR spectra of **2** were recorded in degassed benzene in order to make them well-resolved. The radical **2a** gave a broad 1 : 1 : 1 triplet spectrum, indicating that the splitting is due to the interaction with the nitrogen nucleus. For the radical, the reported value of a_N is 11.4 G (in cyclohexane),[6)] which is in good agreement with this experimental value. The *para*-substituted radicals, **2b** and **2d**, also gave a similarly broad 1 : 1 : 1 triplet spectrum. On the other hand, in the cases of **2c**, **2f**, **2g**, and **2o**, each of the triplet was further split by the interaction with the ring protons, although the splittings were not well-resolved (Fig. 2). In the spectra of **2h**, **2i**, **2k**, **2l**, and **2p**—**r**, however, the splittings were well-resolved (Figs. 3 and 4), and thus the values of a_H were easily determined. The spectra of **2e**, **2j**, **2m**, and **2n** were split by the interaction with the fluorine nuclei and the methyl protons, respectively. However, the spectra were complicated due to superposition with the splittings due to the ring protons,

TABLE. ESR AND VISIBLE SPECTRAL DATA OF DIBENZENESULFENAMIDYL RADICALS (**2**) IN BENZENE AT ROOM TEMPERATURE

Radical	Coupling constant (G)				g-Value	$\lambda_{\max}$ (nm)
	a_N	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p\text{-H}}$		
2a	11.41				2.0082	538
2b	11.45			—	2.0082	545
2c	11.45	0.48	0.20	—	2.0082	541
2d	11.26			—	2.0080	497
2e	11.49			—	2.0082	531
2f	11.37	0.56		—	2.0082	543
2g	11.37	0.56	0.22	—	2.0083	544
2h	11.40	0.57		0.57	2.0081	535
2i	11.40	0.57		0.57	2.0081	537
2j	11.36				2.0083	557
2k	11.29	0.67	0.21	0.67	2.0081	559
2l	11.27	0.67		0.67	2.0081	558
2m	11.44				2.0083	561
2n	11.36				2.0083	568
2o	11.29	0.62		—	2.0082	569
2p	11.27	0.70	0.21	0.70	2.0080	559
2q	11.30	0.70	0.18	0.70	2.0080	558
2r	11.40	0.58	—	0.58	2.0080	531

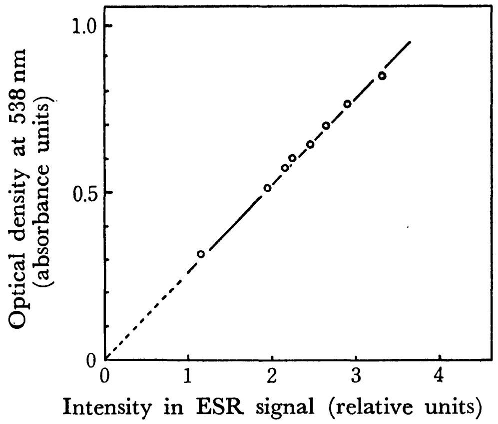


Fig. 1. Plot of ESR signal intensity *vs.* optical density (538 nm) for dibenzenesulfenamidyl radical (**2a**) in benzene at 23 °C.

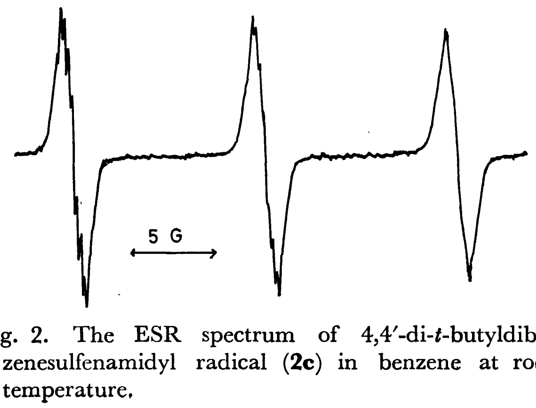


Fig. 2. The ESR spectrum of 4,4′-di-*t*-butyldibenzenesulfenamidyl radical (**2c**) in benzene at room temperature.

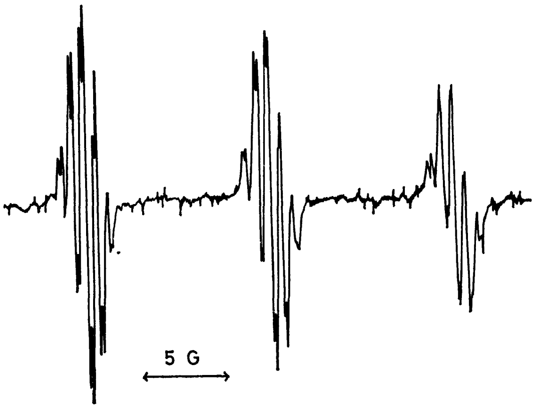


Fig. 3. The ESR spectrum of 2,2′,5,5′-tetrachlorobenzenesulfenamidyl radical (**2q**) in benzene at room temperature.

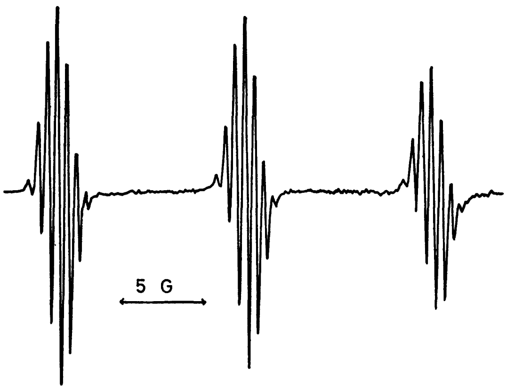


Fig. 4. The ESR spectrum of 3,3′,5,5′-tetrachlorodibenzenesulfenamidyl radical (**2r**) in benzene at room temperature.

and thus poorly resolved. Consequently, the values of a_H and a_N of the radicals could not be determined.

As found in the table, the values of a_N lie in the range of 11.26 to 11.49 G and are almost uninfluenced by the substituents. The values of a_H are very small, indicating that the spin densities of the rings are not large. The unpaired electron is, therefore, distributed mainly on the nitrogen and the two sulfur atoms. The g-values of **2** lie in the range of 2.0080 to 2.0083;⁷⁾ these are large for a nitrogen-centered free radical.⁸⁾ This can be explained in terms of the presence of sulfur atoms possessing a large spin-orbit coupling parameter in the π-system.⁹⁾

Decay Kinetic Studies of Radicals. The radicals **2** are rather long-lived in non-polar solents such as benzene and hexane, and give diaryl disulfide and nitrogen in quantitative yields as final decomposition products. Kinetic studies of the decay of **2** were undertaken at 23 °C in the dark. The results are illustrated in Fig. 5.

According to Barton *et al.*,⁶⁾ a small quantity of **3a** is generated by the coupling reaction of **2a** with phenylthiyl radical in the course of decomposition of **2a**. Since **3a** already decomposes at relatively low temperature (78 °C) into the original radicals, **2a** and phenylthiyl radical, if tribenzenesulfenamides (**3**) are

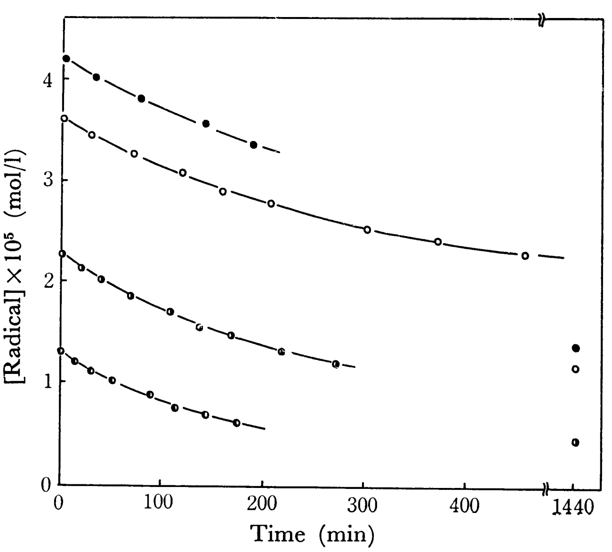
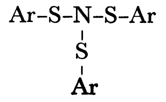


Fig. 5. Decay plots of dibenzenesulfenamidyl radicals at 23 °C.
○; Dibenzenesulfenamidyl radical (**2a**) in degassed benzene, ●; **2a** in benzene exposed to the atmosphere, ◑; 4,4′-dichlorodibenzenesulfenamidyl radical (**2f**) in degassed benzene, ◐; 4,4′-dinitrodibenzenesulfenamidylradical (**2d**) in degassed benzene.

generated in the present kinetic system, the analyses of the kinetic studies may become difficult.



$$\begin{array}{c}\text{Ar-S-N-S-Ar}\\ | \\ \text{S}\\ | \\ \text{Ar}\end{array}$$

3 (**3a**: Ar$=C_6H_5$)

In order to examine whether **3** was generated or not in the present system, thin layer chromatographic analysis was performed for every solution after the kinetic measurement was completed. The substance **3**, however, was not detected at all. Furthermore, the benzene solution of 0.015 mol/l of **3a** gave only 3.0×10^{-6} mol/l of **2a** at 23 °C in the dark (the concentration of **1a** used for the kinetic investigation was 0.054 mol/l). From these results, it seems that **3** scarcely affects the present kinetic studies.

From the figure, it was found that the radicals **2** decay with second-order kinetics (the rate constant **2a**: 1.1, **2d**: 6.8, **2e**: 2.0 l/mol s) and are not sensitive to the atmospheric oxygen. The decay rates decrease in the order of **2d**>**2e**>**2a**, indicating that introduction of electron-withdrawing groups destabilizes the radicals.[2] This may be explained as follows: electron-withdrawing groups stabilize the corresponding hydrazines by reducing the dipolar repulsion between the nirogen atoms.[10] The hydrazines have not yet been isolated, in spite of many attempts,[5] probably because they are very unstable.

Experimental

All melting points were uncorrected. IR and visible spectra were recorded on a Jasco Model IR-G Spectrometer and a Hitachi Recording Spectrometer Model ESP-3T, respectively. Thin layer chromatographic analyses were performed on alumina (Merck Art 1064), using hexane as eluent, and detected by UV-irradiation.

ESR Measurement. ESR spectra were recorded with a JES-ME 3X Spectrometer, equipped with 100 kHz field modulation, at room temperature (23 °C).

Sample preparation was performed as follows: a) dibenzenesulfenamide (**1**, 10 mg) was treated with lead dioxide (0.5 g) and potassium carbonate (0.5 g) in benzene (1.0 ml), and the inorganic compounds were removed by filtration. 0.4 ml of the filtrate was placed in an ESR tube and degassed by three freeze-and-thaw cycles, and then sealed; b) a solution of **1** (5 mg) and di-*t*-butyl peroxide (0.02 ml) in benzene (0.4 ml) was placed in an ESR tube and degassed as above, and then sealed. ESR spectra were recorded under UV-irradiation from a distance of 40 cm using a high pressure mercury lamp (JES-UV-1, 100 W).

Kinetic Studies. Sample preparation was performed according to the procedure b (di-*t*-butyl peroxide was not added). The solution was UV-irradiated for *ca.* 3 min as described above, and the lamp was turned off. Decay rates of radicals were measured at 23 °C in the dark by monitoring the intensity of the ESR signals. Integrations of ESR signals were achieved with a Model JES-ID-2 Integrator, using a benzene solution of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl[4] as a standard.

Materials. The benzene used for the ESR measurements was purified by the usual method: it was shaken with concd sulfuric acid, and washed with dilute potassium carbonate and then water. After drying over anhydrous magnesium sulfate, it was distilled from sodium wire. Commercially available di-*t*-butyl peroxide, benzenethiol, 2-methyl-, 4-methyl-, 4-*t*-butyl-, and 4-chlorobenzenethiols were used without further purification. 4-Fluoro-, 4-bromo-, 2,4-dimethyl-, and 2,4-dichlorobenzenethiols were prepared by treatment of the appropriate benzenes with chlorosulfonic acid, followed by reduction with zinc dust and sulfuric acid.[11,12] 2-Chloro-, 2-bromo-, 3-chloro-, 3-bromo-, 2-methyl-4-chloro-, 2,3-dichloro-, 2,5-dichloro-, and 3,5-dichlorobenzenethiols were prepared from the appropriate diazotized anilines.[13] 4-Nitrobenzenethiol was prepared by the procedure of Price *et al.*[14]

All dibenzenesulfenamides (**1**) except 4,4′-dinitrodibenzenesulfenamide (**1d**) were prepared according to a procedure similar to that in the literature;[15] **1d** was obtained by a modified method. A typical procedure for the preparation of **1** is described below.

Dibenzenesulfenamide (1a). Chlorine gas was passed into dry chlorofrom (200 ml) at −5—0 °C. To the solution was added dropwise benzenethiol (25 g, 0.23 mol) over a period of 1 h, and for an additional 1 h the gas was passed at the same temperature. After chloroform was evaporated, the resulting red oil was distilled, giving pure benzenesulfenyl chloride; 56—57 °C/3 Torr, 24.7 g (0.17 mol). Ammonia gas was passed into dry ether (600 ml) at −40—−50 °C under stirring. To the solution was added dropwise the sulfenyl chloride in dry ether (200 ml) over a period of 2 h. After completion of the addition, the passing of ammonia gas was stopped, and the temperature was gradually raised to room temperature. The formed ammonium chloride was filtered off, and ether was evaporated, giving purple crystals, which were recrystallized from hexane; mp 127—128 °C lit,[15] 127—128 °C), 11.8 g (0.051 mol, 60%).

2-Methyl-(87—88 °C/4 Torr), 4-methyl-(76—78 °C/3 Torr), 4-*t*-butyl-(124—126 °C/7 Torr), and 2,4-dimethylbenzenesulfenyl chlorides (76—78 °C/3 Torr) were purified by distillation. On the other hand, the other sulfenyl chlorides were used for the following steps without any purification after the removal of chloroform.

4,4′-Ditoluenesulfenamide (1b). Mp 98—100 °C (petroleum ether), 29%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 64.18; H, 5.97; N, 5.55%. Calcd for $C_{14}H_{15}NS_2$: C, 64.37; H, 5.77; N, 5.36%.

*4,4′-Di-*t*-butyldibenzenesulfenamide (1c).* Mp 89—91 °C (petroleum ether), 28%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 69.75; H, 7.67; N, 4.21%. Calcd for $C_{20}H_{27}NS_2$: C, 69.50; H, 7.89; N, 4.05%.

4,4′-Difluorodibenzenesulfenamide (1e). Mp 127—129 °C (hexane), 54%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 53.33; H, 3.14; N, 5.24%. Calcd for $C_{12}H_9NF_2S_2$: C, 53.51, H, 3.37; N, 5.20%.

4,4′-Dichlorodibenzenesulfenamide (1f). Mp 132—133 °C (benzene–hexane, lit,[16] 137—140 °C), 71%.

4,4′-Dibromodibenzenesulfenamide (1g). Mp 138—139 °C (methanol), 53%. IR (KBr): 3270 cm^{-1} (NH). Found C, 36.87; H, 2.37; N, 3.70%. Calcd for $C_{12}H_9NBr_2S_2$: C, 36.85; H, 2.32; N, 3.58%.

3,3′-Dichlorodibenzenesulfenamide (1h). Mp 122—123 °C (benzene–hexane), 24%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 47.49; H, 2.95; N, 4.83%. Calcd for $C_{12}H_9NCl_2S_2$: C, 47.68; H, 3.01; N, 4.64%.

3,3′-Dibromodibenzenesulfenamide (1i). Mp 115—117 °C (benzene–hexane), 24%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 37.11; H, 2.23; N, 3.77%. Calcd for $C_{12}H_9NBr_2S_2$: C, 36.85; H, 2.32; N, 3.58%.

2,2′-Ditoluenesulfenamide (1j). Mp 128—130 °C (petroleum ether), 39%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 64.27; H, 5.72; N, 5.31%. Calcd for $C_{14}H_{15}NS_2$: C, 64.37; H, 5.77; N, 5.36%.

2,2′-Dichlorodibenzenesulfenamide (1k). After the removal of ether from the filtrate, to the residue (oil) hexane was added, giving crystalline **1k**, which was recrystallized from methanol, and benzene–hexane; mp 167—169 °C, 21%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 47.57; H, 2.95; N, 4.72%. Calcd for $C_{12}H_9NCl_2S_2$: C, 47.68; H, 3.01; N, 4.64%.

2,2′-Dibromodibenzenesulfenamide (1l). After the removal of ether from the filtrate, to the residue (oil) hexane was added, giving crystalline **1l**, which was recrystallized from methanol, and benzene–hexane; mp 173—174 °C, 31%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 36.86; H, 2.25; N, 3.61%. Calcd for $C_{12}H_9NBr_2S_2$: C, 36.85; H, 2.32; N, 3.58%.

2,2′,4,4′-Dixylenesulfenamide (1m). Mp 116—118 °C (petroleum ether), 49%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 66.33; H, 6.65; N, 5.05%. Calcd for $C_{16}H_{19}NS_2$: C, 66.39; H, 6.62; N, 4.84%.

2,2′-Dimethyl-4,4′-dichlorodibenzenesulfenamide (1n). Mp 144—146 °C (chloroform), 48%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 50.63; H, 3.90; N, 4.21%. Calcd for $C_{14}H_{13}NCl_2S_2$: C, 50.91; H, 3.98; N, 4.24%.

2,2′,4,4′-Tetrachlorodibenzenesulfenamide (1o). After the removal of ether from the filtrate, the crystalline residue was refluxed in methanol (100 ml) for 10 min (not soluble completely) and cooled. The crystals separated were filtered and recrystallized from benzene; mp 185—186 °C, 23%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 38.75; H, 1.86; N, 3.78%. Calcd for $C_{12}H_7NCl_4S_2$: C, 38.83; H, 1.91; N, 3.76%.

2,2′,3,3′-Tetrachlorodibenzenesulfenamide (1p). After the removal of ether from the filtrate, to the oily residue hexane was added, giving crude **1p**, which was filtered, and refluxed in methanol (50 ml) for 10 min (not soluble completely) and cooled. The crystals separated were filtered and recrystallized from benzene–hexane; mp 197—198 °C, 26%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 38.94; H, 1.91; N, 3.76%. Calcd for $C_{12}H_7NClS_2$: C, 38.83; H, 1.91; N, 3.76%.

2,2′,5,5′-Tetrachlorodibenzenesulfenamied (1q). After the removal of ether from the filtrate, to the oily residue hexane was added, giving crude **1q**, which was filtered, and refluxed in methanol (50 ml) for 10 min (not soluble completely) and cooled. The crystals separated were filtered and recrystallized from benzene–hexane; mp 197—198 °C, 20%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 39.06; H, 1.73; N, 3.72%. Calcd for $C_{12}H_7NCl_4S_2$: C, 38.83; H, 1.91; N, 3.76%.

3,3′,5,5′-Tetrachlorodibenzenesulfenamide (1r). Mp 185—186 °C (benzene–chloroform), 16%. IR (KBr): 3270 cm^{-1} (NH). Found: C, 38.75; H, 1.86; N, 3.78%. Calcd for $C_{12}H_7NCl_4S_2$: C, 38.83; H, 1.91; N, 3.76%.

4,4′-Dinitrodibenzenesulfenamide (1d). By a procedure similar to **1a**, 4-nitrobenzenethiol was treated with chlorine and ammonia gases. After the removal of ether from the filtrate, the obtained residue was recrystallized from benzene–hexane, giving 4-nitrobenzenesulfenamide; mp 104—106 °C (lit,[17] 103 °C), 49%.

4-Nitrobenzenesulfenyl chloride, which was prepared from 5.5 g (0.032 mol) of 4-nitrobenzenethiol, was added dropwise at −10—−5 °C under stirring to a solution of 4-nitrobenzenesulfenamide (5.5 g, 0.032 mol) and triethylamine (4.0 g) in acetonitrile (100 ml). After completion of the addition, the reaction mixture was stirred for an additional 30 min at 0 °C, and filtered. After the removal of acetonitrile, the resulting residue was recrystallized repeatedly from methanol, giving yellow brown needles [it was very difficult to obtain pure crystals of **1d**, because bis (4-nitrophenyl) disulfide was always contaminated]; mp 167—169 °C (lit,[17] 155 °C), 0.30 g (9.3 mmol, 3.2%). IR (KBr); 3270 cm^{-1} (NH). Found: C, 44.64; H, 2.64; N, 12.88%. Calcd for $C_{12}H_9N_3O_4S_2$: C, 44.57; H, 2.89; N, 13.00%.

Tribenzenesulfenamide (3a). The compound was prepared according to the literature,[6] mp 62—64 °C (lit,[6] 68 °C).

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