Heteroatom Chemistry
Volume 12, Number 4, 2001

The Structures of Diphenyl(diphenylsulfimido)(nitrido)sulfur(VI) and Diphenyl(diphenylsulfodiimido)(nitrido)sulfur(VI), $Ph_2(X)S=N–(Ph_2)S{\equiv}N$ (X = lone pair, NH)

Takayoshi Fujii, Teruyoshi Fujimori, Shin Miyoshi, Satoru Murotani, Masanori Ohkubo, and Toshiaki Yoshimura

Department of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, Gofuku, Toyama 930-8555, Japan

Received December 14, 2000; revised 18 January 2001

ABSTRACT: *The crystal structures of diphenyl(diphenylsulfimido)(nitrido)sulfur(VI) ($Ph_2S=N–(Ph_2)S{\equiv}N$) (***1***) and diphenyl(diphenylsulfodiimido)(nitrido)sulfur(VI) ($Ph_2(HN=)S=N–(Ph_2)S{\equiv}N$) (***2***) were determined by X-ray crystallographic analysis. The former has a bent S–N–S unit with bridging S–N bond lengths of 1.651(1) and 1.622(1) Å and terminal S–N bond lengths of 1.467(1) Å; the latter compound possesses approximately a u-shaped N–S–N–S–N unit with bridging S–N bond lengths of 1.653(2) and 1.576(2) Å, and terminal S–N bond lengths of 1.456(2) and 1.515(2) Å. Single-point ab initio calculations were also carried out using the data from the crystal structures of* **1** *and* **2**. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:263–268, 2001

INTRODUCTION

Compounds bearing a sulfur-nitrogen bond have been attracting considerable attention due to the possibilities of sulfur possessing different oxidation states and coordination numbers, forming single, double, and triple bonds and being incorporated into acyclic and cyclic systems [1–6]. The SN bond distances in the gas phase range from 1.416 Å in $F_3S{\equiv}N$ [1b] to 1.698 Å in $F_5S–NF_2$ [1c] and in the solid state from 1.357 Å in coordination compound of $F_3S{\equiv}N$, $[Mn(N{\equiv}SF_3)_4(AF_6)_2]$ [1d] to 1.69 Å in $F_5S\text{-}NCR_2$ [1e]. The bond distances are dependent on the coordination number of sulfur and nitrogen and on the oxidation state of sulfur.

We have been investigating the syntheses, structures, and reactivities of organo nitridosulfur compounds bearing an SN triple bond and related compounds [2]. Particularly, we have found that diphenyl(diphenylsulfimido)(nitrido)sulfur(VI) ($Ph_2S=N\text{-}(Ph_2)S{\equiv}N$) (**1**) and diphenyl(diphenylsulfodiimido)(nitrido)sulfur(VI) ($Ph_2(HN=)S=N\text{-}(Ph_2)S{\equiv}N$) (**2**) are obtained in moderate yields by treatment of diphenyl(fluoro)(nitrido)sulfur(VI) ($Ph_2FS{\equiv}N$) with diphenylsulfimide ($Ph_2S=NH$) or the sodium salt of diphenylsulfodiimide ($Ph_2S(=NH)_2$), and these compounds were characterized by spectroscopic means and chemical reactions

---

Dedicated to Professor Naoki Inamoto on the occasion of his 72nd birthday.

Correspondence to: Takayoshi Fujii and Toshiaki Yoshimura.

Contract Grant Sponsor: Ministry of Education, Science, Sports and Culture of Japan.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 09239218.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 10133218.
Contract Grant Number: Grant-in-Aid for Scientific Research No. 11120219.

[2d,i]. Independently, Glemser and Höfer reported the preparation of $\mathrm{F_2S{=}N{-}(F_2)S{\equiv}N}$ and $\mathrm{F_2(O{=})S{=}N{-}(F_2)S{\equiv}N}$ by the reaction of $\mathrm{F_2S({=}NSiMe_3)_2}$ with $\mathrm{SF_4}$ or $\mathrm{OSF_4}$ [1f,g]. For these imidonitridosulfur compounds, the simple valence bond description suggests the presence of triple, double, and single bonds between sulfur and nitrogen atoms, but no structural details of them have been reported. In this article, we describe the crystal and electronic structures of the unique nitridosulfur compounds **1** and **2** using X-ray analyses and quantum chemical calculations (the natural population analysis [NPA] and natural bond orbital [NBO] analyses).

RESULTS AND DISCUSSION

Diphenyl(diphenylsulfimido)(nitrido)sulfur(VI) $[\mathrm{Ph_2S{=}N{-}(Ph_2)S{\equiv}N}]$ (**1**) and diphenyl(diphenylsulfodiimido)(nitrido)sulfur(VI) $[\mathrm{Ph_2(HN{=})S{=}N{-}(Ph_2)S{\equiv}N}]$ (**2**) were prepared by the reaction of diphenyl(fluoro)(nitrido)sulfur(VI) ($\mathrm{Ph_2FS{\equiv}N}$) with diphenylsulfimide ($\mathrm{Ph_2S{=}NH}$) or the sodium salt of diphenylsulfodiimide $[\mathrm{Ph_2S({=}NH)_2}]$ [2d,i]. Suitable crystals for X-ray analysis were obtained by recrystallization of **1** and **2** from acetone/diethyl ether or from acetone/methanol/*n*-hexane, respectively, at room temperature.

The detailed structural analyses of **1** and **2** were performed by X-ray crystallographic analysis. Selected bond distances, bond angles, and torsional angles of **1** and **2** are collected in Tables 1 and 2, respectively. The ORTEP drawings of **1** and **2** are depicted in Figures 1 and 2, respectively.

TABLE 1 Selected Bond Distances, Angles, and Torsional Angles for **1**

Distances (Å)			
S(1)–N(1)	1.467(1)	S(2)–N(2)	1.622(1)
S(1)–N(2)	1.651(1)	S(2)–C(13)	1.794(1)
S(1)–C(1)	1.801(1)	S(2)–C(19)	1.806(1)
S(1)–C(7)	1.810(2)		
Angles (°)			
N(1)–S(1)–N(2)	122.4(7)	C(1)–S(1)–C(7)	100.9(7)
N(1)–S(1)–C(1)	117.5(7)	N(2)–S(2)–C(13)	102.3(6)
N(1)–S(1)–C(7)	114.5(7)	N(2)–S(2)–C(19)	106.3(6)
N(2)–S(1)–C(1)	96.8(6)	C(13)–S(2)–C(19)	99.7(6)
N(2)–S(1)–C(7)	101.2(6)	S(1)–N(2)–S(2)	111.7(7)
Torsional Angles (°)			
S(1)–N(2)–S(2)–C(13)	−150.2(7)		
S(1)–N(2)–S(2)–C(19)	105.7(8)		
S(2)–N(2)–S(1)–N(1)	30.1(1)		
S(2)–N(2)–S(1)–C(1)	158.9(8)		
S(2)–N(2)–S(1)–C(7)	−98.6(8)		

Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 1.

The crystal lattice of **1** consists of $\mathrm{Ph_2S{=}N{-}(Ph_2)S{\equiv}N}$ and water molecules. The oxygen $\cdots$nitrogen ($^{d}\mathrm{O}\cdots\mathrm{N1}$) atom distance is 2.949(1) Å. This value is very close to the sum of the van der Waals radii (2.94 Å) of the two elements [7] and is indicative of the $\mathrm{OH}\cdots\mathrm{N}$ hydrogen bond. The crystal lattice of **2** consists of $\mathrm{Ph_2(HN{=})S{=}N{-}(Ph_2)S{\equiv}N}$, methanol, and two types of water molecules. One water molecule is hydrogen bonded to N1 and N3 of one $\mathrm{Ph_2(HN{=})S{=}N{-}(Ph_2)S{\equiv}N}$ molecule ($^{d}\mathrm{O}\cdots\mathrm{N1}$;

TABLE 2 Selected Bond Distances, Angles, and Torsional Angles for **2**

Distances (Å)			
S(1)–N(1)	1.456(2)	S(2)–N(2)	1.576(2)
S(1)–N(2)	1.653(2)	S(2)–N(3)	1.515(2)
S(1)–C(1)	1.805(3)	S(2)–C(13)	1.795(3)
S(1)–C(7)	1.798(3)	S(2)–C(19)	1.776(3)
Angles (°)			
N(1)–S(1)–N(2)	122.9(1)	N(2)–S(2)–C(13)	108.1(1)
N(1)–S(1)–C(1)	114.7(1)	N(2)–S(2)–C(19)	101.0(1)
N(1)–S(1)–C(7)	116.9(1)	N(3)–S(2)–C(13)	112.7(1)
N(2)–S(1)–C(1)	100.7(1)	N(3)–S(2)–C(19)	104.5(1)
N(2)–S(1)–C(7)	97.6(1)	C(13)–S(2)–C(19)	103.8(1)
C(1)–S(1)–C(7)	100.4(1)	S(1)–N(2)–S(2)	117.5(1)
N(2)–S(2)–N(3)	124.1(1)		
Torsional Angles (°)			
S(1)–N(2)–S(2)–N(3)	−68.02		
S(1)–N(2)–S(2)–C(13)	67.3(2)		
S(1)–N(2)–S(2)–C(19)	175.9(1)		
S(2)–N(2)–S(1)–N(1)	18.7(2)		
S(2)–N(2)–S(1)–C(1)	−110.2(2)		
S(2)–N(2)–S(1)–C(7)	147.6(1)		

Numbers in parentheses are estimated standard deviations in the least significant digits. The atoms-labeling scheme is shown in Figure 2.

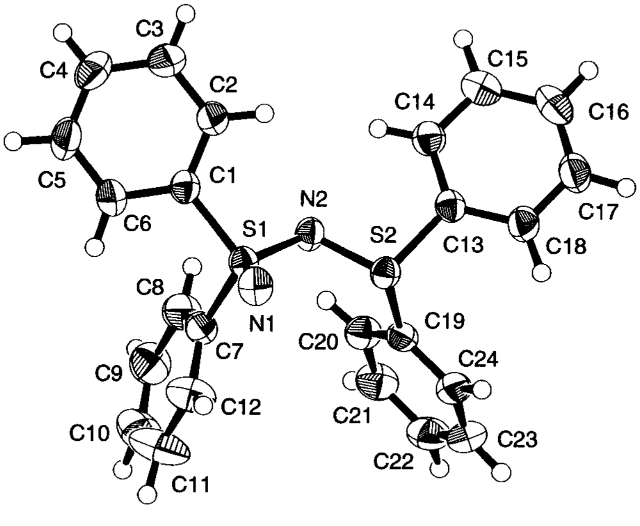

FIGURE 1 Crystal structure of **1**. The monohydrate is omitted.

2.853(3) Å, [d]O···N3; 3.046(3) Å). The other solvent molecules are located in the lattice space between the Ph$_2$(HN$=$)S$=$N–(Ph$_2$)S≡N molecules (distances between O and/or C atoms and nonhydrogen atoms of Ph$_2$(HN$=$)S$=$N–(Ph$_2$)S≡N molecules; $>$ 3.60 Å).

The S1–N1 bond length in **1** is 1.467 Å, which is very close to the SN triple bond length (1.441–1.462 Å) of organonitridosulfur compounds [2c,f,h]. The bridging S–N2 bond lengths are shorter than the sum of the covalent radii of S and N (1.74 Å) [7]. The S2–N2 bond [1.622(1) Å] is somewhat shorter than the S1–N2 bond [1.651(1) Å]. The configuration around the S1 atom in **1** is a slightly distorted tetrahedral structure with two SN and two SC bonds. The bond angles of N1–S1–N2 (122.4(7)°) and N1–S1–C [av. 116.0(7)°] are larger than tetrahedral angle of 109.5°, whereas N2–S1–C [av. 99.0(6)°] and C1–S1–C7 [100.9(7)°] are smaller than this. The N2, C13, and C19 atoms are disposed about a trigonal pyramidal S2 atom, and the bond angles of N2–S2–C [av. 104.3(6)°] and C13–S2–C19 [99.7(6)°] are very similar to that of *N*-tosyldiphenylsulfimide [6b]. The S1–C1 bond is close to eclipsing the S2–C13 bond (torsional angles: C1–S1···S2–C13, ca 2.6°). The other C7–S1···S2–C19 torsion angles (ca. 13°) is also nearly eclipsed. Although the bridging S–N–S bond angle (111.7(7)°) is significantly less than the expected value (120°) of an sp^2 hybridized N2 atom, it is close to that of *N*-tosyldiphenylsulfimide [113.4(45)°] [6b], [Me$_2$SNSMe$_2$]$^+$ Br$^-$ [110.8(2)°] [5b], and [Ph$_2$SNSPhMe]$^+$ [ClO$_4$]$^-$ [109.6(5)°] [5c].

The observed SN bond lengths in **2** fall into three ranges. The terminal S1–N1 and S2–N3 values are 1.456(2) and 1.515(2) Å, and the central S1–N2 and S2–N2 bond distances are 1.653(2) and 1.576(2) Å. The S2–N2 and S2–N3 distances are significantly shorter than that of S1–N2 and is close to that of dimethylsulfodiimide [1.533(4) Å] [6d]. The configuration of S2 in **2** is also a slightly distorted tetrahedral geometry similar to that of dimethylsulfodiimide [6d]. The S1–N2–S2 bond angle of 117.5(1)° in **2** is indicative of sp^2 hybridization at the N2 atom. The torsional angles around S···S of **2** are considerably larger than those of **1** (torsional angles: C1–S1···S2–C13, ca. −41°; C1–S1···S2–C13, ca. −45°; N1–S1···S2–N3, ca. −38°).

In order to understand the electronic structures of **1** and **2**, single-point ab initio calculations with the NPA and NBO analyses [8–10] were carried out at the RHF/6-31G* level using the data from the crystal structures of **1** and **2** (Tables 3 and 4).

As indicated by NPA and NBO analysis, the S–N–S–N unit in **1** has strongly polarized S–N bonds. The NPA charges at the two sulfur and two nitrogen atoms are +1.964 (S1), +1.261 (S2), −1.273 (N1), and −1.334 (N2), respectively. All the carbon atoms bonded to the sulfur atoms are more negatively charged (ranging from −0.263 to −0.335) than the other carbon atoms. The NBO procedure for identifying bonds and lone pairs of the S–N–S–N unit in **1** clearly showed seven σ bonds, one π bond, and five lone pairs. One lone pair at each nitrogen atom occupies essentially a nearly unhybridized 2p orbital (p character; N1, 99.5%; N2, 98.74%). Therefore, Figure 3 (I) shows the best structural representation

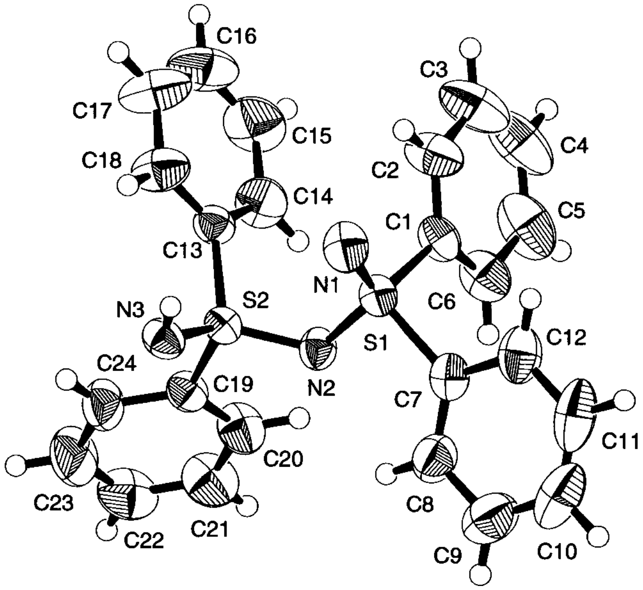

FIGURE 2 Crystal structure of **2**. The dihydrate and methanol molecule are omitted.

TABLE 3 Selected Atomic Charges (NPA) and Occupancy of Lone Pairs (p-LP) and Antibonding (σ*) Orbitals (NBO) for **1**

			Charges		
S(1)	1.964	C(7)	−0.335	C(17)	−0.168
S(2)	1.261	C(8)	−0.159	C(18)	−0.199
N(1)	−1.273	C(9)	−0.183	C(19)	−0.263
N(2)	−1.334	C(10)	−0.175	C(20)	−0.132
C(1)	−0.304	C(11)	−0.195	C(21)	−0.147
C(2)	−0.162	C(12)	−0.138	C(22)	−0.185
C(3)	−0.183	C(13)	−0.243	C(23)	−0.171
C(4)	−0.158	C(14)	−0.164	C(24)	−0.197
C(5)	−0.200	C(15)	−0.195		
C(6)	−0.177	C(16)	−0.168		

		Occupancies	
p-LP(N1)	1.621	σ* (S1–C7)	0.234
p-LP(N2)	1.839	σ* (S2–N2)	0.0207
σ* (S1–N1)	0.048	σ* (S2–C13)	0.061
σ* (S1–N2)	0.151	σ* (S2–C19)	0.080
σ* (S1–C1)	0.168		

The atoms-labeling scheme is shown in Figure 1.

TABLE 4 Selected Atomic Charges (NPA) and Occupancy of Lone Pairs (p-LP) and Antibonding (σ^*) Orbitals (NBO) for **2**

Charges					
S(1)	1.985	C(6)	−0.166	C(16)	−0.159
S(2)	2.092	C(7)	−0.324	C(17)	−0.181
N(1)	−1.291	C(8)	−0.155	C(18)	−0.138
N(2)	−1.375	C(9)	−0.187	C(19)	−0.287
N(3)	−1.136	C(10)	−0.173	C(20)	−0.139
C(1)	−0.328	C(11)	−0.189	C(21)	−0.190
C(2)	−0.143	C(12)	−0.144	C(22)	−0.152
C(3)	−0.188	C(13)	−0.330	C(23)	−0.187
C(4)	−0.180	C(14)	−0.143	C(24)	−0.128
C(5)	−0.188	C(15)	−0.181		

Occupancies			
p-LP(N1)	1.625	σ^* (S1–C7)	0.170
p-LP(N2)	1.825	σ^* (S2–N2)	0.140
p-LP(N3)	1.767	σ^* (S2–N3)	0.073
σ^* (S1–N1)	0.046	σ^* (S2–C13)	0.170
σ^* (S1–N2)	0.150	σ^* (S2–C19)	0.090
σ^* (S1–C1)	0.230		

The atoms-labeling scheme is shown in Figure 2.

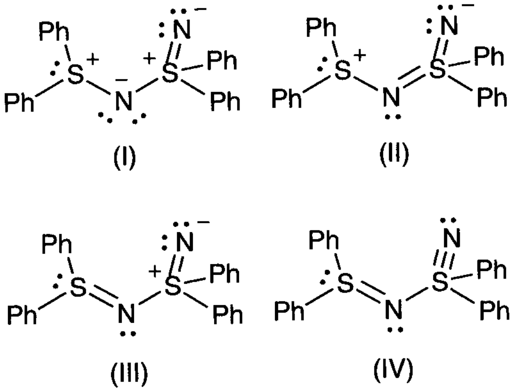

FIGURE 3 Structural representations of **1**.

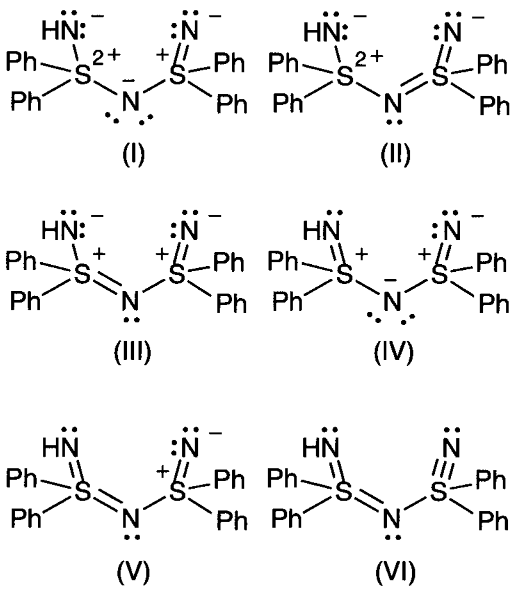

FIGURE 4 Structure representations of **2**.

of **1**. Although significant $\pi_{\mathrm{S1-N1}}$ bonding is present, this is quite polar (81% on N1, 19% on S1) and is primarily delocalized into $\sigma^*_{\mathrm{S1-N2}}$ and $\sigma^*_{\mathrm{S1-C1}}$ antibonding orbitals. NBO second-order perturbation analysis [9,11] of **1** indicates the orbital interaction of p lone pair (p-LP) at the N1 atom (terminal) with the σ^* antibonding orbitals of the S1–N2 (central) and S1–C bonds (p-$\mathrm{LP_{N1}} \rightarrow \sigma^*_{\mathrm{S1-N2}}$, 6.35 kcal mol^{-1}; p-$\mathrm{LP_{N1}} \rightarrow \sigma^*_{\mathrm{S1-C1}}$, 20.49 kcal mol^{-1}; p-$\mathrm{LP_{N1}} \rightarrow \sigma^*_{\mathrm{S1-C7}}$, 61.92 kcal mol^{-1}), and an unevenly five interaction of the central nitrogen lone pair (p-LP) with the $\sigma^*_{\mathrm{S1-N1}}$, $\sigma^*_{\mathrm{S1-C}}$, and $\sigma^*_{\mathrm{S2-C}}$ (p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S1-N1}}$, 2.06 kcal mol^{-1}; $\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S1-C1}}$, 3.26 kcal mol^{-1}; p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S1-C7}}$, 13.41 kcal mol^{-1}; p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S2-C13}}$, 6.03 kcal mol^{-1}; $\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S2-C19}}$, 18.36 kcal mol^{-1}). The interaction of p-$\mathrm{LP_{N2}}$ with $\sigma^*_{\mathrm{S2-C}}$ orbitals is somewhat larger than that of $\sigma^*_{\mathrm{S1-N1}}$ and $\sigma^*_{\mathrm{S1-C}}$ orbitals. These results are apparently indicative of p-$\mathrm{LP_{N}} \rightarrow \sigma^*$ negative hyperconjugation and also explain the three different S–N bond lengths in **1**.

NPA and NBO analysis of **2** also reveals that the N–S–N–S–N unit has strongly polarized S–N bonds and has eight σ bonds, one π bond, and six lone pairs. The $\pi_{\mathrm{S1-N1}}$ orbital is also quite polar (81% on N1, 19% on S1) and is delocalized into $\sigma^*_{\mathrm{S1-N2}}$ and $\sigma^*_{\mathrm{S1-C7}}$ antibonding orbitals. These results suggest that compound **2** is also best viewed as a zwitterion-like structure (1) (Figure 4). Inspection of the NBO second-order perturbation analysis and occupancies (p-$\mathrm{LP_{N}}$, $\sigma^*_{\mathrm{S-N}}$, and $\sigma^*_{\mathrm{S-C}}$) results shows p-LP → σ^* negative hyperconjugation. The interaction energies between p-LP at each terminal nitrogen atom (N1 and N2) and σ^* orbitals of the S–N and S–C bonds are 5.08 (p-$\mathrm{LP_{N1}} \rightarrow \sigma^*_{\mathrm{S1-N2}}$), 60.51 (p-$\mathrm{LP_{N1}} \rightarrow \sigma^*_{\mathrm{S1-C1}}$), 22.96 (p-$\mathrm{LP_{N1}} \rightarrow \sigma^*_{\mathrm{S1-C7}}$), 37.19 (p-$\mathrm{LP_{N3}} \rightarrow \sigma^*_{\mathrm{S2-N2}}$), 23.03 (p-$\mathrm{LP_{N3}} \rightarrow \sigma^*_{\mathrm{S2-C13}}$), 1.11 kcal mol^{-1} (p-$\mathrm{LP_{N3}} \rightarrow \sigma^*_{\mathrm{S2-C19}}$). The interaction with $\sigma^*_{\mathrm{S2-N3}}$ (p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S2-N3}}$, 18.97 kcal mol^{-1}) and $\sigma^*_{\mathrm{S2-C13}}$ (p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S2-C13}}$, 17.95 kcal mol^{-1}) orbitals is significantly larger than $\sigma^*_{\mathrm{S1-N1}}$ (p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S1-N1}}$, 1.50 kcal mol^{-1}), $\sigma^*_{\mathrm{S1-C1}}$ (p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S1-C1}}$, 11.47 kcal mol^{-1}), and $\sigma^*_{\mathrm{S1-C7}}$ (p-$\mathrm{LP_{N2}} \rightarrow \sigma^*_{\mathrm{S1-C7}}$, 3.74 kcal mol^{-1}) orbitals. These results indicate the three different ranges of S–N bond lengths in **2**.

EXPERIMENTAL

All solvents and reagents were obtained commercially and were further purified by general methods when necessary.

Diphenyl(diphenylsulfimido)(nitrido)sulfur(VI)

(**1**) and diphenyl(diphenylsulfodiimido)(nitrido) sulfur(VI) (**2**) were prepared according to the methods reported in our previous articles [2d,i].

X-Ray Crystal Structure Analysis of 1

The single crystals were obtained by recrystallization from acetone-ether. Diffraction data were measured with the ω-2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). A total of 6505 reflections was collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92) [12] and expanded using Fourier techniques (DIRDIF) [13]. The nonhydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4941 observed reflections ($I > 3.00\sigma(I)$) and 322 variable parameters converged with the unweighted and weighted agreement factors equal to $R = (\Sigma\|Fo| - |Fc\|)/(\Sigma|Fo|) = 0.034$; $R_w = [(\Sigma\omega\ (|Fo| - |Fc|)^2/\Sigma\omega Fo^2)]^{1/2} = 0.050$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.19/−0.19 e$^-$/Å^3, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1999). Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 153988 for compound **1**.

X-Ray Crystal Structure Analysis of 2

The single crystals were obtained by recrystallization from acetone-ether. Diffraction data were measured with the ω-2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). A total of 8441 reflections was collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92) [12] and expanded using Fourier techniques (DIRDIF) [13]. The nonhydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4941 observed reflections ($I > 3.00\sigma(I)$), and 307 variable parameters converged with the unweighted and weighted agreement factors equal to $R = (\Sigma\|Fo| - |Fc\|)/(\Sigma|Fo|) = 0.046$; $R_w = [(\Sigma\omega\ (|Fo| - |Fc|)^2/\Sigma\omega Fo^2)]^{1/2} = 0.064$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.25/−0.18 e$^-$/Å^3, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1999). Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 153989 for compound **2**.

Ab Initio Calculation of 1 *and* 2

Single-point ab initio calculations using the data from crystal structures of **1** and **2** were carried out using the GAUSSIAN 94 program package [10] on IBM RS/6000 SP computers. The calculations were carried out at the Hartree-Fock level of theory with the 6-31G* basis set.

REFERENCES

[1] (a) Glemser, O.; Mews, R. Angew Chem Int Ed Engl 1980, 19, 883–899, and references therein; (b) Krichhoff, W. H.; Wilson, E. B., Jr., J Am Chem Soc 1962, 84, 334–336; (c) Haase, J.; Oberhammer, H.; Zeil, W.; Glemser, O.; Mews, R. Z Naturforsh 1971, 26a, 1333–1335; (d) Buss, B.; Clegg, W.; Hartmann, G.; Jones, P. G.; Mews, R.; Noltemeyer, M.; Sheldrick, G. M. J Chem Soc Dalton Trans 1981, 61–63; (e) Sitzmann, M. E.; Gilardi, R. D. J Fluorine Chem 1993, 63, 203–215; (f) Glemser, O.; Höfer, R. Angew Chem Int Ed Engl 1971, 10, 815; (g)] Glemser, O.; Höfer, R. Z Naturforsh 1974, 29b, 121–122.

[2] (a) Yoshimura, T.; Kita, H.; Takeuchi, K.; Takata, E.; Hasegawa, K.; Shimasaki, C.; Tsukurimichi, E. Chem Lett 1992, 1433–1436; (b) Yoshimura, T.; Takata, E.; Miyake, T.; Shimasaki, C.; Hasegawa, K.; Tsukurimichi, E. Chem Lett 1992, 2213–2216; (c) Yoshimura, T.; Hamata, K.; Imado, M.; Hamata, K.; Tomoda, K.; Fujii, T.; Morita, H.; Shimasaki, C.; Ono, S.; Tsukurimichi, E.; Furukawa, N.; Kimura, T. J Org Chem 1997, 62, 3802–3803; (d) Ohkubo, M.; Fujii, T.; Ono, S.; Morita, H.; Yoshimura, T.; Horn, E.; Sato, S. Chem Lett 1997, 153–154; (e) Yoshimura, T.; Fujii, T.; Hamata, K.; Imado, M.; Morita, H.; Ono, S.; Horn, E. Chem Lett 1998, 1013–1014; (f) Yoshimura, T.; Ohkubo, M.; Fujii, T.; Kita, H.; Wakai, Y.; Ono, S.; Morita, H.; Shimasaki, C.; Horn, E. Bull Chem Soc Jpn 1998, 71, 1629–1637; (g) Yoshimura, T.; Dong, T.; Fujii, T.; Ohkubo, M.; Sakuta, M.; Wakai, Y.; Ono, S.; Morita, H.; Shimasaki, C. Bull Chem Soc Jpn 2000, 73, 957–965; (h) Horn, E.; Dong, T.; Fujii, T.; Yoshimura, T.; Shimasaki, C. Z Kristallogr NCS 2000, 215, 357–358; (i) Yoshimura, T.; Fujii, T.; Murotani, S.; Miyoshi, S.; Fujimori, T.; Ohkubo, M.; Ono, S.; Morita, H. J Organomet Chem 2000, 611, 272–279.

[3] (a) Hänssgen, W.; Roelle, W. J Organomet Chem 1973, 63, 269–278; (b) Borrmann, T.; Zibarev, A. V.; Lork, E.; Knitter, G.; Chen, S.-J.; Watson, P. G.; Cutin, E.; Shakirov, M. M.; Stohrer, W.-D.; Mews, R. Inorg Chem 2000, 39, 3999–4005, and references therein.

[4] (a) Roesky, H. W. Angew Chem Int Ed Engl 1979, 18, 91–97; (b) Gleiter, R. Angew Chem Int Ed Engl 1981, 20, 444–451; (c) Manners, I. Angew Chem Int Ed Engl 1996, 35, 1602–1621; (d) Chivers, T.; Gibson, M. P.; Parvez, M.; Vargas-Baca, I. Inorg Chem 2000, 39, 1697–1704.

[5] (a) Oae, S.; Numata, T.; Yoshimura, T. In The Chemistry of the Sulfonium Groups, Part 2; Patal, S., Stir-

ling, C. J., Eds.; Wiley: Chichester, U.K., 1981; Chapter 15 and references therein; (b) Griffin, A. M.; Sheldrick, G. M. Acta Crystallogr 1975, B31, 863–894; (c) Nishikawa, Y.; Natsuura, Y.; Kakudo, M.; Akasaka, T.; Furukawa, N.; Oae, S. Chem Lett 1978, 447–450; (d) Oae, S.; Furukawa, N. Sulfilimines and Related Derivatives; America Chemical Society: Washington, DC, 1983; and references therein.

[6] (a) Sass, R. L. Acta Crystallogr 1960, 13, 320–324; (b) Kálmán, A. Acta Crystallogr 1967, 22, 501–506; (c) Kálmán, A.; Duffin, B.; Kucsman, A. Acta Crystallogr 1971, B27, 586–594; (d) Kálmán, A.; Sasvári, K.; Kucsman, A. Acta Crystallogr 1973, B29, 1241–1244; (e) Weeb, N. C.; Gloss, R. A. Tetrahedron Lett 1967, 1043–1047; (f) Cook, R. E.; Glick, M. D.; Rigau, J. J.; Johnson, C. R. J Am Chem Soc 1971, 93, 924–928; (g) Glass, R. S.; Duchek, J. R. J Am Chem Soc 1976, 98, 965–969; (h) Roesky, H. W.; Fuess, M. D. H.; Bats, J. W. Angew Chem Int Ed Engl 1978, 17, 58–59.

[7] Emsley, J. The Elements, 3rd ed.; Oxford University Press: Oxford, U.K., 1998.

[8] Glendeling, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO, version 3.1.

[9] Reed, A. E.; Curtis, L. A.; Weinhold, F. Chem Rev 1988, 88, 899–926, and references therein.

[10] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewshi, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacomb, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, C.; Gonzalez, C.; Popel, J. A. GAUSSIAN 94, revision E. 2; Gaussian, Inc.: Pittsburgh, PA, 1995.

[11] (a) Reed, A. E.; Schleyer, P. v. R.; J Am Chem Soc 1987, 109 7362–7371; (b) Reed, A. E.; Schleyer, P. v. R. Inorg Chem 1988, 27 3969–3987; (c) Reed, A. E.; Schleyer, P. v. R. J Am Chem Soc 1990, 112 1434–1445, and references therein.

[12] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. J Appl Cryst 1994, 27, 435.

[13] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory, University of Nijmegen: The Netherlands, 1994.