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Journal of Organometallic Chemistry 611 (2000) 272–279

Journal of Organo metallic Chemistry

The structures of $[Ph_2XS–N–SPh_2NH]^+$ cations (X=NH, O)

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Received 1 March 2000; received in revised form 10 April 2000; accepted 10 April 2000

Abstract

Diphenyl(diphenylsulfodiimidoyl)(nitrido)sulfur(VI) (**2**) and diphenyl(diphenylsulfoximidoyl)(nitrido)sulfur(VI) (**3**) ($Ph_2XS–N–SNPh_2N$, X = NH, O) were prepared by the reaction of diphenyl(fluoro)(nitrido)sulfur(VI) (Ph_2FSN) with sodium salts of diphenyl-sulfodiimide ($Ph_2S(NH)_2$) and -sulfoximide (Ph_2OSNH). The nitrido-sulfur complexes **2** and **3** are considerably basic ($pK_a = 7.86$ and 7.60, respectively). Treatment of **2** and **3** with perchloric acid afforded quantitatively the corresponding μ-*aza*-bis[diphenyl(imido)sulfur(V)] perchlorate (**4**) and μ-*aza*-[diphenyl(imido)]-[diphenyl(oxo)]disulfur(V) perchlorate (**5**) ($[Ph_2XS–N–SPh_2NH]^+[ClO_4]^-$, X = NH, O). The crystal structures of **4** and **5** were determined by X-ray crystallographic analysis. The former has essentially C_2 symmetry with an S–N–S bond angle of 120.3(2)°, bridging S–N bond lengths of 1.595(3) and 1.604(3) Å, and terminal S–N bond lengths of 1.509(3) and 1.497(3); the latter cation is an unsymmetrically substituted oxygen analog with an S–N–S bond angle of 123.1(2)°, and bridging S–N bond lengths of 1.607(4) and 1.568(4) Å, terminal S–N and S–O bond lengths of 1.501(3) and 1.438(2) Å. Single-point ab initio calculations were also carried out using the data from the crystal structures of **4** and **5**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: $[PH_2NHS–N–SPH_2NH]^+$ cation; $[PH_2OS–N–SPH_2NH]^+$ cation; Nitridosulfur(VI); X-ray crystallographic analysis; Single-point ab initio calculation

1. Introduction

The chemistry of cationic species with nitrogen bridges between sulfur atoms shows some interesting and fascinating features [1,2]. Numerous binary S–N cations have been prepared and structurally characterized [1,3]. In contrast to neutral and anionic S–N compounds, S–N cations do not undergo explosive nitrogen elimination reactions. Moreover, $[SN]^+$ and $[S_2N]^+$ have been proven to be very useful building blocks in sulfur–nitrogen chemistry [4–6]. Mews reported that the reaction of $[SN]^+[MF_6]^-$ (M = As, Sb) with SCl_2 lead to the corresponding $[ClS–N–SCl]^+[MF_6]^-$ (M = As, Sb) [5]. Brook, Passmore and White et al. reported the synthesis of $[XS–N–SX]^+[AsF_6]^-$ (X = Cl, Br) and $[F_2S–N–SF_2]^+[AsF_6]^-$ by the halogenation of $[S_2N]^+[AsF_6]^-$ [6]. The latter structure was determined to have approximately C_{2v} symmetry with essentially eclipsed fluorine–sulfur bonds as viewed along the sulfur–sulfur axis by X-ray crystallographic analysis [6] and its ab initio theoretical calculation was performed by Klapötke et al. [7]. On the other hand, synthesis of $[Me_2S–N–SMe_2]^+[Br]^-$ possessing four carbon ligands has been reported [8]. Independently, we reported that the reaction of *N*-halo-diphenylsulfilimide (Ph_2SNX, X = Cl, Br) with sulfide (R_2S, R = Me, Ph, p-tol, Et; R,R = $(CH_2)_4$, $(CH_2)_5$) and sulfoxide (R_2SO, R = Me, Ph, p-tol) affords the corresponding $[Ph_2S–N–SR_2]^+[X]^-$ and $[Ph_2S–N–SR_2O]^+[X]^-$ [9]. The X-ray structures of $[Me_2S–N–SMe_2]^+[Br]^-$ and $[Ph_2S–N–SPhMe]^+[ClO_4]^-$ have been reported [10]. These cations possess a bent S–N–S unit with an approximately tetrahedral angle at nitrogen. The two S–N bond lengths in the former cation are essentially identical, whereas those in the latter are significantly different and the cationic charge should be localized on one sulfur atom.

We recently described the synthesis of dialkyl- and diphenyl-(diphenylsulfimidoyl)(nitrido)sulfur(VI)

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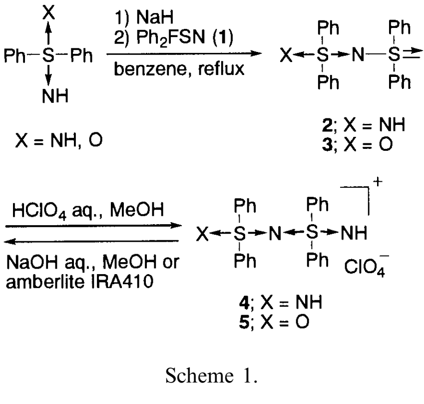
PII: S0022-328X(00)00448-4

(Ph_2S–N–SR_2N, R = Me, Et, Ph) and their cations $[Ph_2S\text{–}N\text{–}SR_2NH]^+$, and established that diphenyl(fluoro)(nitrido)sulfur(VI) (Ph_2FSN) (**1**) is a potentially useful building block in S–N–S chemistry [11]. Moreover, the X-ray structure of $[Ph_2S\text{–}N\text{–}SEt_2NH]^+$ $[ClO_4]^-$ revealed that the two S–N distances of S–N–S unit are significantly different and the compound should be regarded as an aminosulfonium-type structure. In a further extension of these studies, we prepared diphenyl(diphenylsulfodiimidoyl)(nitrido)sulfur(VI) (**2**) and diphenyl(diphenylsulfoximidoyl)(nitrido)sulfur(VI) (**3**) (Ph_2XS–N–SPh_2N, X = NH, O) by the reaction of **1** with sodium salts of diphenyl-sulfodiimide ($Ph_2S(NH)_2$) and -sulfoximide (Ph_2OSNH). These nitrido-sulfur **2** and **3** are considerably basic. Treatment of **2** and **3** with perchloric acid afforded quantitatively the corresponding μ-*aza*-bis[diphenyl(imido)sulfur(V)] perchlorate (**4**) and μ-*aza*-[diphenyl(imido)]-[diphenyl(oxo)]disulfur(V) perchlorate (**5**) ($[Ph_2XS\text{–}N\text{–}SPh_2NH]^+[ClO_4]^-$, X = NH, O). In this paper we report the preparation and the crystal structures of a new type of $[Ph_2XS\text{–}N\text{–}SPh_2NH]^+$ cations (X = NH, O). Furthermore, in order to understand the electronic structures of these cationic species, single-point ab initio calculations were carried out using the data from the crystal structures of **4** and **5**.

2. Results and discussion

*2.1. Synthesis of compounds **2**–**5***

Previously, we briefly reported on the synthesis of diphenyl(diphenylsulfimidoyl)(nitrido)sulfur(VI) (Ph_2S–N–SPh_2N) by the reaction of Ph_2FSN (**1**) with diphenylsulfilimide (Ph_2SNH) [11]. Because of the lower nucleophilicity of sulfodiimide and sulfoximide than Ph_2SNH [12], the corresponding sodium salt of diphenyl-sulfodiimide ($Ph_2S(NH)_2$) or -sulfoximide (Ph_2OSNH) prepared by deprotonaion initially with sodium hydride in benzene was allowed to react with **1** under reflux conditions. After the solvent was removed, the residue was washed with *n*-hexane, and the corresponding diphenyl(diphenylsulfodiimidoyl)(nitrido)sulfur(VI) (**2**) or diphenyl(diphenylsulfoximidoyl)(nitrido)sulfur(VI) (**3**) (Ph_2XS–N–SPh_2N, X = NH, O) was obtained as a white powder in 70% yield or a white powder in 68% yield, respectively (Scheme 1). ^1H and ^{13}C-NMR, IR, and elemental analyses were consistent with the structure of **2** and **3**. Interestingly, ^1H and ^{13}C-NMR spectra of **2** showed only one set of phenyl groups in the temperature range −50 to +150°C in $CDCl_3$ and DMSO-d_6. This is probably due to the fast tautomeric proton exchange between the two terminal nitrogen atoms like the enol from of acetylacetone, though the chelate structure of the present system is not clear.



Scheme 1.

The nitrido-sulfur **2** and **3** are considerably basic. The p*K*a values of the conjugate acids of **2** and **3** are 7.86 and 7.60 by potentiometric titration using 0.1 M hydrochloric acid at 25°C. Therefore, μ-*aza*-bis[diphenyl(imido)sulfur(V)] perchlorate (**4**) and μ-*aza*-[diphenyl(imido)]-[diphenyl(oxo)]disulfur(V) perchlorate (**5**) ($[Ph_2XS\text{–}N\text{–}SPh_2NH]^+[ClO_4]^-$, X = NH, O) were readily prepared in essentially quantitative yields by the treatment of **2** or **3** with a slightly excess perchloric acid ($HClO_4$) in MeOH–H_2O at room temperature (Scheme 1). These cations **4** and **5** are thermally stable and can be converted back to the **2** and **3** quantitatively by treatment with aqueous NaOH (1 M) or passing a methanolic solution of them through a column of ion-exchange resin IRA-410 (OH^- form).

*2.2. X-ray structures of **4** and **5***

The detailed structural analyses of $[Ph_2NHS\text{–}N\text{–}SPh_2NH]^+[ClO_4]^-$ **4** and $[Ph_2OS\text{–}N\text{–}SPh_2NH]^+$ $[ClO_4]^-$ (**5**) were performed by X-ray crystallographic analysis. Selected bond distances, bond angles, and torsional angles of **4** and **5** are collected in Tables 1 and 2, respectively. The ORTEP drawings of **4** and **5** are depicted in Figs. 1 and 2, respectively. In the **4** or **5** unit cell, the shortest perchlorate anion···none-hydrogen atom distance is 3.315(6) Å ($d_{O\cdots C24}$) or 3.207(6) Å ($d_{O\cdots C24}$, disordered perchlorate anion), respectively. These value are longer than sum of the van der Waals radii (2.95 Å) [13].

The structure of **4** has essentially C_2 symmetry. The two phenyl and one imido groups are disposed approximately each tetrahedral-like sulfur atom. The bond lengths of two bridging S–N, two terminal S–N, and four S–C are not significantly different from one another. Although the average bridging S–N bond length (1.600(3) Å) in **4** is shorter than the sum of the covalent radii of S and N (1.74 Å) [13], it is almost the same as the average S–N bond length in $[Me_2S\text{–}N\text{–}SMe_2]^+$ (1.635(4) Å) [10a], $[Ph_2S\text{–}N\text{–}SPhMe]^+$ (1.635(1) Å)

Table 1
Selected bond distances (Å), angles (°), and torsional angles (°) for **4** [a]

Distances			
S(l)–N(l)	1.509(3)	S(2)–N(2)	1.604(3)
S(l)–N(2)	1.595(3)	S(2)–N(3)	1.497(3)
S(l)–C(I)	1.778(4)	S(2)–C(13)	1.782(4)
S(l)–C(7)	1.777(4)	S(2)–C(19)	1.782(3)
Angles			
N(1)–S(1)–N(2)	123.0(2)	N(2)–S(2)–C(13)	98.4(2)
N(I)–S(1)–C(1)	114.2(2)	N(2)–S(2)–C(19)	109.2(2)
N(I)–S(1)–C(7)	105.6(2)	N(3)–S(2)–C(13)	115.2(2)
N(2)–S(1)–C(l)	100.2(2)	N(3)–S(2)–C(19)	104.5(2)
N(2)–S(1)–C(7)	108.4(2)	C(13)–S(2)–C(19)	106.2(2)
C(l)–S(1)–C(7)	104.0(2)	S(1)–N(2)–S(2)	120.3(2)
N(2)–S(2)–N(3)	122.5(2)		
Torsional angles			
S(1)–N(2)–S(2)–N(3)	51.0(3)	S(2)–N(2)–S(1)–N(1)	56.1(3)
S(1)–N(2)–S(2)–C(13)	178.1(2)	S(2)–N(2)–S(1)–C(1)	−176.0(2)
S(1)–N(2)–S(2)–C(19)	−71.3(2)	S(2)–N(2)–S(1)–C(7)	−67.5(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The atom labeling scheme is shown in (Fig. 1).

Table 2
Selected bond distances (Å), angles (°) and torsional angles (°) for **5** [a]

Distances			
S(1)–N(1)	1.501(3)	S(2)–O(1)	1.438(2)
S(1)–N(2)	1.607(4)	S(2)–N(2)	1.568(4)
S(1)–C(1)	1.782(4)	S(2)–C(13)	1.759(4)
S(1)–C(7)	1.780(4)	S(2)–C(19)	1.776(4)
Bond angles			
N(1)–S(1)–N(2)	123.1(2)	O(1)–S(2)–C(13)	111.1(2)
N(1)–S(1)–C(1)	115.7(2)	O(1)–S(2)–C(13)	108.0(2)
N(1)–S(1)–C(7)	105.4(2)	N(2)–S(2)–C(13)	100.8(2)
N(2)–S(1)–C(1)	98.1(2)	N(2)–S(2)–C(19)	109.7(2)
N(2)–S(1)–C(7)	107.3(2)	C(13)–S(2)C–(19)	106.5(2)
C(1)–S(1)–C(1)	106.1(2)	S(1)–N(2)–S(2)	123.1(2)
O(1)–S(2)–N(2)	119.9(2)		
Torsional angles			
S(1)–N(2)–S(2)–O(1)	−47.3(4)	S(2)–N(2)–S(1)–N(1)	47.0(4)
S(1)–N(2)–S(2)–C(13)	−169.5(3)	S(2)–N(2)–S(1)–C(1)	−175.0(3)
S(1)–N(2)–S(2)–C(l9)	78.5(3)	S(2)–N(2)–S(1)–C(7)	75.3(3)

[a] Numbers in parentheses are estimated as standard deviations in the least significant digits. The atom labeling scheme is shown in (Fig. 2).

[10b], and $[Ph_2S–N–SEt_2NH]^+$ (1.619(3) Å) [11]. The average terminal S–N bond length in **4** is 1.503(3) Å, which is significantly shorter than that of the bridging S–N and is very close to those of $[Ph_2S–N–SEt_2NH]^+$ (1.510(4) Å) [11] and $Me_2S(NH)_2$ (1.533(4) Å) [14]. This suggests that the terminal S–N bonds have a higher bond order than the bridging S–N bonds.

The S1–N2–S2 bond angle of 120.3(2)° in **4** is indicative of sp^2 hybridization on the N_2 atom, and in valence bond terms suggests that the bonding may be represented by structure (I)–(IV) (Fig. 3). The S1–C1 and S2–C13 bonds lie in the S1–N2–S2 plane and are close to eclipsing each S–N bond of S1–N2–S2 unit (trosional angles: S1–N2–S2–C13, 178.1(2)°, S2–N2–S1–C1, –176.0(2)°, C1–S1···S2–C13, approximately 2.7°). The other N–S–S–C torsion angles (average approximately 19°) are nearly eclipsed. The related $[Ph_2S–N–SEt_2NH]^+$ [11] and $[Ph_3P–N–PPh_3]^+$ [15] do not have this eclipsed structure (average torsional angles:

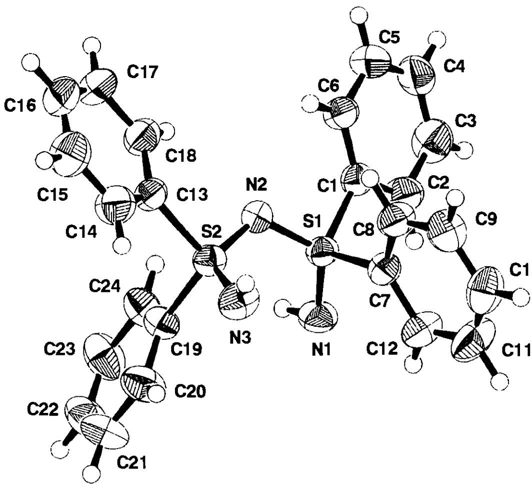


Fig. 1. ORTEP view of **4**. The perchlorate anion is omitted.

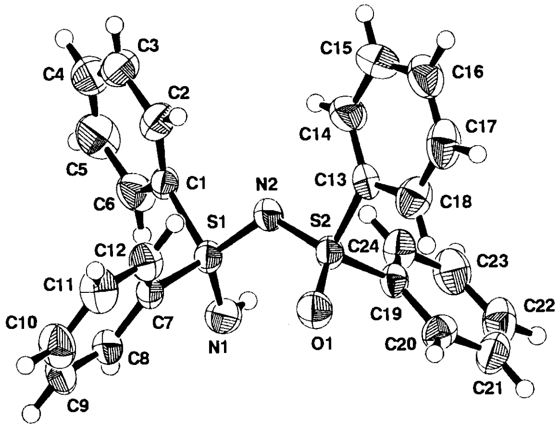


Fig. 2. ORTEP view of **5**. The perchlorate anion is omitted.

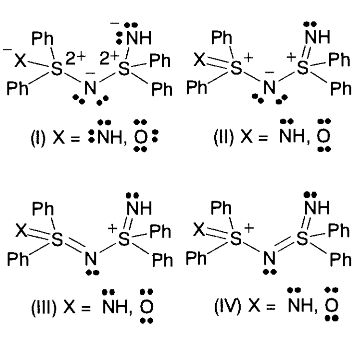


Fig. 3. Structural representations of the **4** and **5**.

C–S···S–C, approximately 28°, C–P···P–C, approximately 42°), whereas $[Ph_2S–N–PPh_3]^+$ has an eclipsed structure (average torsional angle: C–S···P–C, approximately 7°), with the third phenyl group attached to the phosphorus atom lying in the S–N–P plane [16].

The cation **5** is an unsymmetrically substituted isoelectronic compound with an S–N–S bond angle of 123.1(2)°, and bridging S–N bond lengths of 1.607(4) (d_{S1-N2}) and 1.568(4) Å (d_{S2-N2}). The terminal S1–N1 and S2–O1 bond lengths are 1.501(3) and 1.438(2) Å, respectively. These values are very close to those of $Me_2S(NH)_2$ (d_{S-N}; 1.533(4) Å) [14] and Me_2OSNH (d_{S-N}; 1.521(3) Å, d_{S-O}; 1.437(3) Å) [17]. Similar to the conformation of **4**, the nitrogen atom of **5** also lies in one of the *syn* C–S···S–C planes, but the torsional angles around the S···S of **5** are somewhat larger than those of **4** (torsional angles: N1–S1–S2–C19, approximately 31°; C7–S1–S2–O1, approximately 29°; C1–S1–S2–C13, approximately 20°).

2.3. *Ab initio calculation of **4** and **5***

In order to understand the electronic structures of **4** and **5**, single-point ab initio calculations with the natural population analysis (NPA) and natural bond orbital (NBO) analyses [18] were carried out using the data from the crystal structures of **4** and **5**. The calculations were carried out at the RHF/6-31G* level using GAUSSIAN-94 [19] (Table 3 and Table 4).

Table 3
Selected atomic charges (NPA) and occupancy of lone pairs (p-LP) and antibonding (σ*) orbitals (NIBO) for **4** [a]

Charges					
S(1)	2.092	C(6)	−0.149	C(16)	−0.136
S(2)	2.080	C(7)	−0.329	C(17)	−0.166
N(I)	−1.229	C(8)	−0.150	C(18)	−0.145
N(2)	−1.340	C(9)	−0.180	C(19)	−0.318
N(3)	−1.144	C(10)	−0.127	C(20)	−0.130
C(I)	−0.339	C(11)	−0.176	C(21)	−0.166
C(2)	−0.138	C(12)	−0.116	C(22)	−0.131
C(3)	−0.175	C(13)	−0.323	C(23)	−0.780
C(4)	−0.127	C(14)	−0.155	C(24)	−0.156
C(5)	−0.174	C(15)	−0.163		
Occupancies					
p-LP(N1)	1.748	σ* (Sl-C7)	0.110		
p-LP(N2)	1.825	σ* (S2-N2)	0.167		
p-LP(N3)	1.742	σ* (S2-N3)	0.060		
σ* (S1–N1)	0.061	σ* (S2-C13)	0.134		
σ* (S1–N2)	0.159	σ* (S2-C19)	0.120		
σ* (S1–C1)	0.143				

[a] The atom labeling scheme is shown in Fig. 1.

Table 4
Selected atomic charges (NPA) and occupancy of tone pairs (p-LP) and antibonding σ* orbitals (NBO) for **5** [a]

Charges					
S(1)	2.098	C(6)	−0.147	C(16)	−0.127
S(2)	2.306	C(7)	−0.323	C(17)	−0.173
O(1)	−1.024	C(8)	−0.122	C(18)	−0.130
N(1)	−1.208	C(9)	−0.180	C(19)	−0.354
N(2)	−1.355	C(I0)	−0.117	C(20)	−0.166
C(1)	−0.336	C(11)	−0.174	C(21)	−0.165
C(2)	−0.141	C(12)	−0.143	C(22)	−0.127
C(3)	−0.172	C(13)	−0.351	C(23)	−0.168
C(4)	−0.122	C(14)	−0.140	C(24)	−0.131
C(5)	−0.172	C(15)	−0.176		
Occupancies					
p-LP(O1)	1.861	σ* (Sl–Cl)	0.141		
p-LP(O1)	1.823	σ* (Sl–C7)	0.108		
p-LP(N1)	1.739	σσ* (S2–O1)	0.081		
p-LP(N2)	1.824	σ* (S2–N2)	0.122		
σ* (S1–N1)	0.057	σ* (S2–C13)	0.119		
σ* (S1–N2)	0.170	σ* (S2–C19)	0.134		

[a] The atom labeling scheme is shown in (Fig. 2)

As indicated by NPA and NBO analysis, the N–S–N–S–N unit in **4** has strongly polarized S–N bonds. The NPA charges at the two sulfur and three nitrogen atoms are + 2.092 (S1), + 2.080 (S2), − 1.229 (N1), − 1.340 (N2), and − 1.144 (N3), respectively. All the carbon atoms bonded to the sulfur atoms are negatively charged (ranging from − 0.318 to − 0.339). The NBO procedure for identifying bonds and lone pairs of N–S–N–S–N unit in **4** clearly showed eight σ bonds and six lone pairs. One lone pair at each nitrogen atom is essentially a nearly unhybridized 2p orbital (p character; N1, 99.3; N2, 99.8; N3, 99.7%). Therefore, Fig. 3 (I) shows the best Lewis representation of **4**. NBO second-order perturbation analysis [18c, 20] of **4** indicates two strong orbital interaction of p lone pair (p-LP) at each terminal nitrogen atom with the antibonding σ^* orbitals of the S–N(central) and S–C bonds (p-$LP_{N1} \rightarrow \sigma^*_{S1-N2}$, 38.11 kcal mol^{-1}; p-$LP_{N1} \rightarrow \sigma^*_{S1-C1}$, 26.45 kcal mol^{-1}; p-$LP_{N3} \rightarrow \sigma^*_{S2-N2}$, 46.61 kcal mol^{-1}; p-$LP_{N3} \rightarrow \sigma^*_{S2-C13}$, 12.82 kcal mol^{-1}), and four fairly strong interaction of central nitrogen lone pair (p-LP) with $\sigma^*_{S-N(\text{terminal})}$ and σ^*_{S-C} (p-$LP_{N2} \rightarrow \sigma^*_{S1-N1}$, 13.77 kcal mol^{-1}; $LP_{N2} \rightarrow \sigma^*_{S1-C7}$, 14.74 kcal mol^{-1}; p-$LP_{N2} \rightarrow \sigma^*_{S2-N3}$, 12.42 kcal mol^{-1}, p-$LP_{N2} \rightarrow \sigma^*_{S2-C19}$, 15.54 kcal mol^{-1}). The NBO occupancies for p-LP_N, σ^*_{S-N}, and σ^*_{S-C} in **4** are 1.748 (p-LP_{N1}), 1.825 (p-LP_{N2}), 1.742 (p-LP_{N3}), 0.061 (σ^*_{S1-N1}), 0.159 (σ^*_{S1-N2}), 0.143 (σ^*_{S1-C1}), 0.110 (σ^*_{S1-C7}), 0.167 (σ^*_{S2-N2}), 0.060 (σ^*_{S2-N3}), 0.134 (σ^*_{S2-C13}), 0.120 (σ^*_{S2-C19}), respectively, and the ratio between the total lone pair occupancy depletion at nitrogen atoms and the total 3d orbital population (by NPA) at sulfur atoms is 0.979: 0.26 [20c]. These results are apparently indicative of p-$LP_N \rightarrow \sigma^*$ negative hyperconjugation and also explain the two different set of S–N bond lengths in **4**.

NPA and NBO analysis of **5** also reveals that the O–S–N–S–N unit has strongly polarized S–O and S–N bonds, and has eight σ bonds and seven lone pairs. These results suggest that the cation **5** is also best viewed as zwitterion-like structure I (Fig. 3). Inspection of the NBO second-order perturbation analysis and occupancies (p-LP_O, p-LP_N, σ^*_{S-N}, and σ^*_{S-C}) results shows p-LP → σ^* negative hyperconjugation. The four strong interaction energies between p-LP at central nitrogen atom (N2) and σ^* orbitals of the S–N, S–O and S–C bonds are 9.71 (p-$LP_{N2} \rightarrow \sigma^*_{S1-N1}$), 15.56 (p-$LP_{N2} \rightarrow \sigma^*_{S1-C7}$), 14.01 (p-$LP_{N2} \rightarrow \sigma^*_{S2-O1}$), and 17.35 kcal mol^{-1} (p-$LP_{N2} \rightarrow \sigma^*_{S2-C19}$). The interaction with σ^*_{S2-O1} and σ^*_{S2-C19} orbitals is somewhat larger than σ^*_{S1-N1} and σ^*_{S1-C7} orbitals. These results explain the two slightly different bridging S–N lengths.

The present results provide the synthesis and structure of the $[Ph_2NHS-N-SPh_2NH]^+$ and $[Ph_2OS-N-SPh_2NH]^+$ cations, and further work in this area is currently underway in our laboratory.

3. Experimental

All NMR spectra were obtained with a JEOL-LNM 400 spectrometer with TMS as an internal standard. Mass spectra were recorded with a JEOL-JMS700 mass spectrometer. IR spectra were recorded with a Horiba FT-710 spectrometer. Melting points were measured with a Yanaco-MP-J3. Elemental analyses were performed on a Yanaco MT-5 CHN CORDER. The X-ray crystallographic analyses were performed on a Rigaku AFC7R four-circle diffractometer using graphite monochromated Mo–K_α radiation at 296 K.

All solvents and reagents were dried and purified according to the standard methods. Diphenyl(fluoro)(nitrido)sulfur(VI) (**1**) was prepared according to Ref. [21].

3.1.1. Synthesis of diphenyl(diphenylsulfodiimidoyl)-(nitrido)sulfur(VI) (2)

A suspension of sodium hydride (72 mg, 3.0 mmol) and diphenylsulfodiimide (432 mg, 2.0 mmol) in benzene (10 ml) was refluxed under an argon atmosphere for 30 min. The reaction mixture was cooled at room temperature (r.t.) and a solution of **1** (438 mg, 2.0 mmol) in benzene (10 ml) was added to the reaction mixture. The reaction mixture was refluxed and stirred overnight. The solvent was removed under reduced pressure, and the residue was washed with hexane and then recrystallized from acetone–hexane to give a white powder of complex **2** (583 mg, 70%): m.p. 143–144°C.

Elemental Analysis: Anal. Found: C, 69.34, H, 5.17, N, 10.12. Calc. for $C_{24}H_{21}N_3S_2$: C, 69.36; H, 5.09; N, 10.11%. ^{1}H-NMR (400 MHz, $CDCl_3$, r.t.): δ 7.38–7.46 (m, 12H), 7.99–8.02 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$, r.t.): δ 126.8, 128.8, 131.6, 147.0. ^{1}H-NMR (400 MHz, $CDCl_3$, − 50°C): δ 7.44–7.53 (m, 12H), 8.03–8.05 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$, − 50°C): δ 126.6, 128.8, 131.8, 146.8. ^{1}H-NMR (400 MHz, DMSO-d_6, 150°C): δ 7.40–7.50 (m, 12H), 7.87–7.92 (m, 8H). ^{13}C-NMR (400 MHz, DMSO-d_6, 150°C): δ 125.6, 127.8, 130.4, 147.4. IR (KBr, cm^{-1}) 3055, 1287, 1074, 958. FABMS (m/z) 416 ($[M+H]^+$).

3.1.2. Synthesis of diphenyl(diphenylsulfoximidoyl)-(nitrido)sulfur(VI) (3)

A suspension of sodium hydride (72 mg, 3.0 mmol) and diphenylsulfoximide (434 mg, 2.0 mmol) in benzene (10 ml) was refluxed under an argon atmosphere for 30 min. The reaction mixture was cooled at r.t. and a solution of **1** (438 mg, 2.0 mmol) in benzene (10 ml) was added to the reaction mixture. The reaction mixture was refluxed and stirred overnight. The solvent was removed under reduced pressure, and the residue was washed with hexane and then recrystallized from acetone–hexane to give a white powder of complex **3** (566 mg, 68%): m.p. 105–106°C.

Table 5
Crystallographic data and refinement details for **4**

Formula	$C_{24}H_{22}ClN_3O_4S_2$
Formula weight	516.03
Crystal size (mm^3)	$0.50\times0.40\times0.30$
Crystal system	Monoclinic
Space group	*Cc* (No. 9)
a (Å)	15.201(3)
b (Å)	10.267(2)
c (Å)	16.182(3)
β (°)	104.56(1)
V (Å^3)	2444.5(7)
D_{calc} (g cm$^{-1)}$	1.402
$F_{(000)}$	1072.00
Z	4
μ (cm$^{-1)}$	3.63
Number of data	3685
Number of unique data ($I>3.00\sigma(I)$)	3562
$2\theta_{\max}$ (°)	60
p-Factor	0.0300
R	0.033
R_w	0.040
Goodness-of-fit indicator	1.38

Elemental analysis: Anal. Found: C, 68.90; H, 4.90; N, 6.63. Calc. for $C_{24}H_{20}N_2OS_2$: C, 69.20; H, 4.84; N, 6.72%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37–7.56 (m, 12H), 7.96–8.03 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 126.5, 127.8, 128.4, 129.3, 130.8, 133.2, 140.7, 150.6. IR (KBr, cm^{-1}): 1316, 1225, 991.

*3.1.3. Synthesis of μ-aza-bis[diphenyl(imido)sulfur(V)] perchlorate (**4**)*

To a solution of **2** (415 mg, 1 mmol) in MeOH (5 ml) at r.t. was added 60% perchloric acid (167 μl) and stirred for 1 h. The solution was diluted with water and extracted three times with CH_2Cl_2, the extract was dried over magnesium sulfate, and the solvent was removed to give **4** (501 mg, 97%). Further purification by recrystallization from acetone–ether produced colorless crystals of **4**. m.p. 163–164°C.

Elemental analysis: Anal. Found: C, 55.90; H, 4.17; N, 8.10. Calc. for $C_{24}H_{22}ClN_2O_4S_2$: C, 55.86; H, 4.30; N, 8.14%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56–7.63 (m, 12H), 8.09–8.11 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 127.5, 130.1, 134.5, 139.2. IR (KBr, cm^{-1}) 3226, 1177, 1026, 977.

*3.1.4. Synthesis of μ-aza-[diphenyl(imido)]-[diphenyl(oxo)]disulfur(V) perchlorate (**5**)*

To a solution of **3** (416 mg, 1 mmol) in MeOH (5 ml) at r.t. was added 6 N hydrochloric acid (167 μl) and was then stirred for 1 h. The solution was diluted with water and extracted three times with CH_2Cl_2. The extract was dried over magnesium sulfate, and the solvent was removed to give **5** (512 mg, 99%). Further purification by recrystallization from MeOH–ether produced colorless crystals of **5**. m.p. 184–185°C.

Elemental analysis: Anal. Found: C, 55.79; H, 4.07; N, 5.37. Calc. for $C_{24}H_{21}ClN_2O_5S_2$: C, 55.75; H, 4.09; N, 5.42%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60–7.70 (m, 12H), 8.11–8.15 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 127.6, 127.9, 130.2, 130.5, 134.9, 135.4, 136.7, 138.6. IR (KBr, cm^{-1}) 3202, 1237, 1088, 992.

*3.2. Measurement of pK_a value of **2** and **3***

In 50.0 ml of distilled water, 0.19×10^{-3} mol of **2** or **3** was dissolved and its pH value was measured with a Horiba pH meter model F-13 at 25°C. To this solution 25×0.1 ml portions of 0.973 N hydrochloric acid was added, and the pH values were measured after each addition. The pK^+_{BH} values were obtained with the following equation: $\mathrm{p}Ka^+_{\mathrm{BH}} = \mathrm{pH} + \log([\mathrm{BH}^+] - [\mathrm{H}^+]/[\mathrm{B}] + [\mathrm{H}^+])$; where $[\mathrm{B}]$ = the concentration of the unprotonated thiazyne, $[\mathrm{BH}^+]$ = the concentration of the protonated thiazyne (obtained from the quantity of the hydrochloric acid added) and $[\mathrm{H}^+]$ = the proton activity.

*3.3. X-ray crystal structure analysis of **4***

Single crystals were obtained by recrystallization from acetone–ether. Diffraction data were measured using the ω–2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.7107$ Å). A total of 3685 reflections were collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR-92) [22] and expanded using Fourier techniques (DIRDIF) [23]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2521 observed reflections ($I>3.00\sigma(I)$) and 305 variable parameters converged with the unweighted and weighted agreement factors equal to $R = (\Sigma\|F_o| - |F_c\|)/(\Sigma|F_o|) = 0.033$; $R_w = [(\Sigma\,\omega(|F_o| - |F_c|)^2/\Sigma\,\omega F_o^2)]^{1/2} = 0.040$. The maximum and minimum peaks on the final difference Fourier map corresponded to $0.14/-0.14$ e Å^{-3}, respectively. All calculations were performed using the TEXSAN crystallographic software package from the Molecular Structure Corporation (1985 and 1999). The crystal data and final atomic coordinates are listed in Table 5.

*3.3.2. X-ray crystal structure analysis of **5***

Single crystals were obtained by recrystallization from acetone–ether. Diffraction data were measured using the ω–2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.7107$ Å). A total of 3876 reflections were collected. The data were corrected for

Table 6
Crystallographic data and refinement details for **5**

Formula	$C_{24}H_{21}ClN_2O_5S_2$
Formula weight	517.01
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.50$
Crystal system	Monoclinic
Space group	$P2_1$ (#4)
a (Å)	9.782(3)
b (Å)	9.021(2)
c (Å)	13.653(2)
β (°)	97.81(2)
V (Å^3)	1193.6(4)
D_{calc} (g cm^{-1})	1.438
F(000)	536.00
Z	2
μ (cm^{-1})	3.74
Number of data	3876
Number of unique data ($I > 3.00\sigma(I)$)	3837
$2\theta_{max}$ (°)	60
p-Factor	0.0300
R	0.036
R_w	0.041
Goodness-of-fit indicator	1.33

Lorentz and polarization effects. The structure was solved by direct methods (SIR-92) [22] and expanded using Fourier techniques (DIRDIF) [23]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2430 observed reflections ($I > 3.00\sigma(I)$) and 335 variable parameters converged with the unweighted and weighted agreement factors equal to $R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|) = 0.036$; $R_w = [(\Sigma\, \omega(|F_o| - |F_c|)^2/\Sigma\, \omega F_o^2)]^{1/2} = 0.041$. The maximum and minimum peaks on the final difference Fourier map corresponded to $0.19/-0.15$ e Å^{-3}, respectively. All calculations were performed using the TEXSAN crystallographic software package from the Molecular Structure Corporation (1985 and 1999). The crystal data and final atomic coordinates are listed in Table 6.

3.4. Ab initio calculation of **4** and **5**

Single-point ab initio calculations using data from the crystal structures of **4** and **5** were carried out using the GAUSSIAN-94 program package [19] on IBM RS/6000 SP computers. The calculations were carried out at the Hartree–Fock level of theory with the 6-31G* basis set.

4. Supplementary material

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142664 for compound **4** and CCDC no. 142665 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (A) of the Chemistry of Inter-element Linkage Chemistry (Nos. 09239218, 10133218, and 11120219) from the Ministry of Education, Science, Sports and Culture. We thank Dr Ohgi Takahashi at the University of Tsukuba for helpful discussions.

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