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Molecular structures of cyclic sulfilimines without and with intramolecular sulfur-oxygen interaction: an X-ray study

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Abstract

3-Phenylbenzo[1.3.2]dithiazolium ylide 1.1 dioxide (**1**) and its *o*-methoxycarbonyl derivative (**2**) have been prepared and their structures established by X-ray crystallography from diffractometer data. Compound **1** ($C_{12}H_9NO_2S_2$) crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.664(1)$, $b = 7.881(1)$, $c = 12.437(2)$ Å, $\alpha = 98.81(1)$, $\beta = 97.44(1)$, $\gamma = 113.05(1)°$, $V = 580.9(4)$ Å^3, $Z = 2$, $D_c = 1.51$ g.cm^{-3} and $\mu(\mathrm{CuK}\alpha) = 4.00$ mm^{-1}. Compound **2** ($C_{14}H_{11}NO_4S_2$) crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 7.620(1)$, $b = 8.887(1)$, $c = 20.022(2)$ Å, $V = 1355.9(5)$ Å^3, $Z = 4$, $D_c = 1.57$ g.cm^{-3} and $\mu(\mathrm{CuK}\alpha) = 3.65$ mm^{-1}. The crystal structures were solved by direct methods and refined to $R = 0.062$ for **1** and $R = 0.028$ for **2**, using 1663 and 1424 observed reflections, respectively. In the cyclic *N*-sulfonyl sulfilimines **1** and **2** the characteristic bond distances and bond angles involving S(IV) and S(VI) atoms do not differ significantly from those found earlier for acyclic sulfilimines. Owing to S(IV) ··· O(carbonyl) close contact the sulfur(IV) atom in **2** exhibits a sulfuran-like configuration with almost linear (171°) N = S(IV) ··· O array (1.61 + 2.68 = 4.29 Å). The conformations of **1** and **2** have similar features. In both cases the five-membered dithiazolium ring is practically planar and the two aryl rings about sulfur(IV) atom are nearly perpendicular to the C_{ar}–S(IV)–C_{ar} plane ("butterfly conformation"). In contrast with acyclic sulfilimines, the benzene ring connected to S(VI) atom is constrained to be coplanar with the S(VI)–N–S(IV) plane (Koch and Moffitt's case I of conjugation).

Keywords: X-ray crystallography; Cyclic sulphilimines; Sulphur–oxygen interaction

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1. Introduction

The actual conformation in a great number of organosulfur compounds is controlled by sulfur-oxygen close contact [1] in which the S ··· O interatomic distance is shorter than the sum of the van der Waals radii (3.25 Å). This non-bonded interaction between sulfur and oxygen atoms is promoted by an X–S(Q)–Csp^2–Csp^2–Csp^2=O type conjugation between the heteroatoms lying in the 1,5 position and also by an electronegative "counter-atom", e.g. X = F, O or N [2]. Except for the single case of an *o*-methoxy-carbonyl-substituted S–alkyl–S–aryl–N–sulfonylsulfilimine

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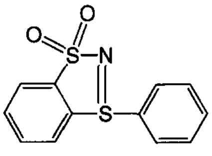
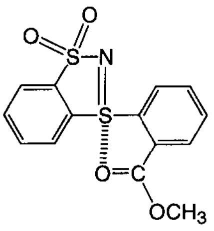
(**3**, see ref. [3]), the 1,5-interaction involving N–S(IV)···O close contact has not yet been studied, to our knowledge, in detail. For this reason cyclic S,S-diaryl–N–sulfonylsulfilimines without and with *o*-methoxycarbonyl substituent (**1** and **2**) were prepared and investigated by X-ray diffraction. Results may show how the N=S(IV)···O type interaction, if it exists, can influence the actual conformation of sulfilimines in which the S(IV)=N–SO_2 group is a part of a heterocycle. It may also be examined how the conjugation in the C_{ar}–S(IV)=N–S(VI)O_2–C_{ar} moiety of sulfilimines is modified in cyclic models. Some representatives of this type of sulfilimines were synthesized earlier without investigating their molecular structures in detail [4].



1



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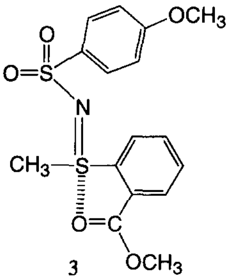

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2. Model compounds

3-Phenylbenzo[1.3.2]dithiazolium ylide 1,1-dioxide (**1**) was obtained by a synthesis starting from 2-iodobenzenesulfonamide (*o*-I-C_6H_4-SO_2NH_2) which was coupled with thiophenol (C_6H_5SH) to give 2-phenyl-thiobenzenesulfonamide (C_6H_5S–C_6H_4–SO_2NH_2). This compound was converted (S-oxidation followed by intramolecular dehydration) to the cyclic sulfilimine **1** by a slight modification of a known method [4c].

3-(2-Methoxycarbonylphenyl)benzo[1.3.2]dithiazolium ylide 1,1-dioxide (**2**) was prepared from 2-(2-aminosulfonyl)phenylsulfinyl benzoic acid (*o*–NH_2SO_2–C_6H_4–SO–C_6H_4–CO_2H–*o*, see ref. [5]) by intramolecular dehydration [6] to give the free acid precursor of **2** from which the ester **2** was obtained by O-methylation with diazomethane.

3. Experimental

3.1. Materials

3.1.1. General

Melting points were determined on a Boetius micro melting point apparatus. IR spectra were taken on a Specord IR 75 (Zeiss, Jena) spectrophotometer. Solvents were purified and dried by the usual methods; pyridine by distillation over P_2O_5. Products were dried over P_2O_5 and/or KOH.

3.1.2. 3-Phenylbenzo[1.3.2]dithiazolium ylide 1,1-dioxide (1)

A mixture of ethylene glycol (46 cm^3), 10 N aqueous KOH (54 cm^3), 2–iodobenzenesulfonamide [5] (28.3 g, 100 mmol), thiophenol (11.0 g, 100 mmol) and copper bronze (0.5 g) was boiled on an oil bath (180–190°C) under nitrogen atmosphere for 6 h, then poured into water (350 cm^3) and acidified with cc HCl. An oily precipitate formed, which solidified on rubbing. The solid was triturated with water in a mortar then filtered off. The crude product (23.5 g) was crystallized from an ethanol–water mixture (200–200 cm^3), filtered off, then dried to yield 2-phenylthiobenzenesulfonamide (16.1 g, 61%), mp 111–113°C (111–112°C in ref. [4c]). This compound (13.3 g, 50 mmol) was converted to **1** by bromine (see ref. [4c]; the reaction mixture was made alkaline with 5 N aqueous KOH before pouring it into water). The crude product (11.3 g, 86%; mp 185–190°C) was crystallized from dry ethanol (600 cm^3; charcoal) to give **1** in white prisms (7.0 g), mp 191–193°C (191–192°C in ref. [4c]).

3.1.3. 3-(2-Methoxycarbonylphenyl)benzo[1.3.2]-dithiazolium ylide 1,1-dioxide (2)

To a solution of 2-(2-aminosulfonyl)phenylsulfinyl benzoic acid hemihydrate [5] (7.2 g, 21.5 mmol) in hot dry pyridine (80 cm^3) was added acetic anhydride (10 cm^3, 105 mmol). The white crystalline product formed immediately was filtered off, washed with pyridine and ether then dried to give the pyridinium salt of the free acid precursor of the title compound **2** (CO_2H instead of $COOCH_3$) (7.15 g, 86%); ν_{max} (KBr) (cm^{-1}) 972s (SNS). The pyridinium salt (2.0 g, 5.2 mmol) was dissolved in 5% aqueous $KHCO_3$ (20 cm^3) and the ice-cold solution was acidified with 2 N aqueous HCl. The precipitate formed was filtered off, washed with water and crystallized from a methanol–water mixture to yield 3-(2-carboxyphenyl)benzo[1.3.2]dithiazolium ylide 1,1-dioxide (see formula **2** with CO_2H group instead of $COOCH_3$; 1.2 g, 75%), mp 260–262°C, and after resolidification 330–332°C (327–332°C with decomposition in ref. [6]). (Found: C, 50.5; H, 3.2; N, 4.3; O, 21.2; S, 20.6%. Calcd. for $C_{13}H_9NO_4S_2$: C, 50.80; H, 2.95; N, 4.56; O, 20.82; S, 20.86%; MW, 307.34). ν(KBr) (cm^{-1}) 1685vs (C=O), 990s (SNS).

The above 2-carboxyphenyl derivative (3.8 g, 12.4 mmol) was suspended in dry methanol (50 cm^3) then treated with a slight excess of diazomethane dissolved in ether. After 30 min the remaining diazomethane was decomposed by an ethereal solution of acetic acid. The solvent was evaporated and the residue was crystallized from methanol (900 cm^3) to yield white crystals of compound **2** (2.2 g, 55%), mp 258–268°C. (Found: C, 52.1; H, 3.4; N, 4.4; O, 20.1; S, 20.7%. Calcd. for $C_{14}H_{11}NO_4S_2$: C, 52.32; H, 3.45; N, 4.36; O, 19.91; S, 19.95%; MW, 321.37). ν(KBr) (cm^{-1}) 1698vs (C=O), 985s and 960sh (SNS).

3.2. Crystal structure determinations

Table 1 summarizes the relevant data concerning the crystal structure analyses.

Table 1
Crystal and relevant X-ray data for compounds **1** and **2**

	1	**2**
Formula	$C_{12}H_9NO_2S_2$	$C_{14}H_{11}NO_4S_2$
MW	263.34	321.38
Melting point (°C)	191–193	258–268
Crystal size (mm)	0.10 × 0.13 × 0.40	0.08 × 0.20 × 0.25
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a (Å)	6.664(1)	7.620(1)
b (Å)	7.881(1)	8.887(1)
c (Å)	12.437(2)	20.022(2)
α (deg)	98.81 (1)	90
β (deg)	97.44(1)	90
γ (deg)	113.05(1)	90
V (Å^3)	580.9(4)	1355.9(5)
Z	2	4
D_c (g cm^{-3})	1.51	1.57
Absorption coefficient (mm^{-1})	4.00	3.65
$F(000)$	272	664
Temperature (K)	293(2)	293(2)
Number of the unique reflections	2081	1556
Data/restraints/parameters	1663/0/191	1424/0/190
Goodness-of-fit on F	2.72	0.748
Final R indices [$I > 3.0\sigma(I)$]	0.062	0.028
Final R_w	0.076	0.040
R indices (all data)	0.071	0.034
ρ_{max} in ΔF map (eÅ^{-3})	0.50(9)	0.19(4)

Intensities for **1** and **2** were recorded on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated CuK_α ($\lambda = 1.5418$ Å) radiation by using an ω–2Θ scan in the range $1.5° < \Theta < 75°$. For each crystal, three standard reflections were monitored every hour. No decay correction was applied in either case. Cell constants (see Table 1) for each crystal were determined by least squares refinement of diffractometer angles for 25 automatically centred reflections. Data were corrected for Lorentz and polarization effects. The phase problems were solved by direct methods by using the MULTAN program [7]. For both crystals empirical absorption corrections (DIFABS [8]) were calculated at the end of the isotropic least-squares refinement for the positional parameters of non-hydrogen atoms. Full matrix least-squares refinement minimized $\sum w(\Delta F^2)$ with $w = 4F_0^2/\sigma^2(F_0^2)$, using the reflections taken with the criteria $I > 3\sigma(I)$. In each case, the fractional coordinates of the hydrogen atoms were generated from assumed geometries. The hydrogen parameters were refined isotropically for **1**, whereas for **2** they were only included in structure factor calculations without refinement by using the isotropic displacement parameters fixed to the corresponding heavy atom with the usual way. Scattering factors were taken from standard tables [9]. Anomalous dispersion effects were included in F_c calculations, the f' and $\Delta f''$ values were those of Cromer [10]. All calculations were performed on a PDP-11/34 minicomputer by using the Enraf-Nonius SDP program package [11].

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) with ESDs (in parentheses) for non-hydrogen atoms in molecules *1* and *2*

	x/a	y/b	z/c	U_{eq}^{a}
Molecule **1**				
S1	0.2593(1)	0.8103(1)	0.77403(8)	0.0408(3)
S2	−0.1640(1)	0.7460(1)	0.68617(8)	0.0463(3)
O1	−0.2511(4)	0.8019(4)	0.5924(2)	0.063(1)
O2	−0.3032(4)	0.7019(4)	0.7661(2)	0.061(1)
N1	0.0871(4)	0.9011(4)	0.7401(2)	0.047(1)
C1	0.1007(5)	0.5709(5)	0.6948(3)	0.040(2)
C2	−0.1100(5)	0.5477(5)	0.6450(3)	0.041(2)
C3	−0.2565(6)	0.3741(5)	0.5762(3)	0.050(1)
C4	−0.1900(8)	0.2315(6)	0.5614(3)	0.056(2)
C5	0.0223(7)	0.2552(5)	0.6139(3)	0.056(1)
C6	0.1702(6)	0.4279(5)	0.6814(3)	0.047(2)
C7	0.2563(3)	0.7740(5)	0.9134(3)	0.040(2)
C8	0.4208(6)	0.7275(6)	0.9617(3)	0.056(2)
C9	0.4253(8)	0.7046(6)	1.0709(3)	0.067(1)
C10	0.2769(8)	0.7313(7)	1.1287(3)	0.062(2)
C11	0.1177(7)	0.7829(8)	1.0801(3)	0.068(2)
C12	0.1049(7)	0.8035(6)	0.9717(3)	0.058(2)
Molecule **2**				
S1	0.54697(7)	0.49145(6)	0.22291(2)	0.0339(3)
S2	0.69786(8)	0.54158(7)	0.10095(3)	0.0391(3)
O1	0.6767(2)	0.4423(2)	0.04503(9)	0.0547(1)
O2	0.8449(2)	0.6419(2)	0.0960(1)	0.0547(1)
O3	0.3075(2)	0.5219(2)	0.32031(9)	0.0508(1)
O4	0.3661(2)	0.5831(2)	0.42645(9)	0.0506(9)
N1	0.6937(2)	0.4460(2)	0.1689(1)	0.0403(1)
C1	0.4245(3)	0.6244(2)	0.1735(1)	0.0343(1)
C2	0.5044(3)	0.6482(3)	0.1128(1)	0.0357(1)
C3	0.4320(3)	0.7491(3)	0.0673(1)	0.0420(1)
C4	0.2789(4)	0.8218(3)	0.0843(1)	0.049(1)
C5	0.1982(3)	0.7948(3)	0.1454(1)	0.0460(1)
C6	0.2685(3)	0.6955(3)	0.1909(1)	0.0403(1)
C7	0.6491(3)	0.6215(2)	0.2818(1)	0.0357(1)
C8	0.5767(3)	0.6431(2)	0.3453(1)	0.0380(1)
C9	0.6677(4)	0.7312(3)	0.3912(1)	0.049(2)
C10	0.8245(4)	0.7974(3)	0.3743(1)	0.058(2)
C11	0.8927(4)	0.7766(4)	0.3101(2)	0.056(2)
C12	0.8067(3)	0.6860(3)	0.2647(1)	0.045(1)
C13	0.4022(3)	0.5762(3)	0.3615(1)	0.0410(1)
C14	0.1944(4)	0.5281(4)	0.4460(1)	0.066(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Fractional atomic coordinates and mean vibrational parameters (U_{eq}) with LS-computed standard deviations are listed in Table 2.

List of structure factors and anisotropic displacement parameters for non-hydrogen atoms and hydrogen atomic positions are available from the authors (A. Kálmán) on request.

4. Results and discussion

The solid-state conformations established for molecules **1** and **2** are shown in Figs. 1 and 2. The enantiomers with *S* configuration at the chiral sulfur atom were chosen for perspective representation. In Table 3 selected bond lengths, bond angles and torsion angles (with ESDs in parentheses), including data that characterize S···O close contacts, are listed for the cyclic

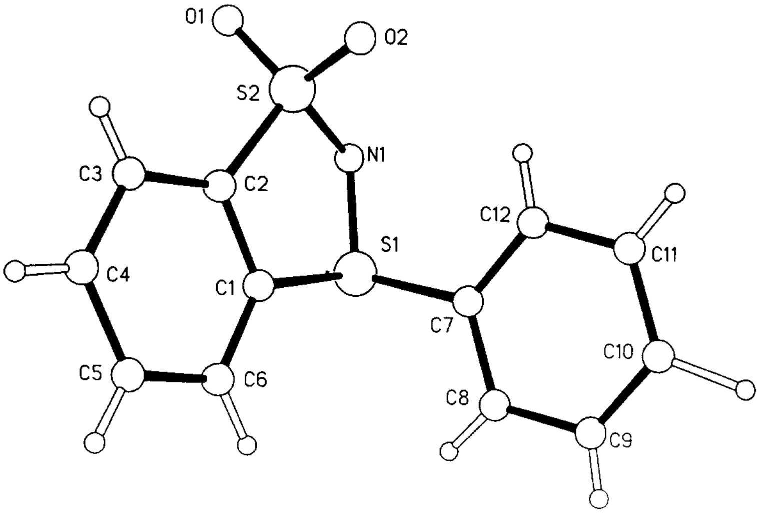

Fig. 1. Solid-state conformation for compound **1** as obtained by X-ray diffraction with atom numbering scheme for non-hydrogen atoms.

sulfilimines **1** and **2** as well as for an acylic analogue, *S*-(2-methoxycarbonylphenyl)-*S*-methyl-*N*-(4-methoxyphenylsulfonyl)-sulfilimine (**3**) investigated earlier [3]. Geometry data quoted in the text are rounded off; the torsion angles are marked by numbering the ϕ symbols as is shown in Table 3.

4.1. Hetero ring with sulfimide moiety

The five-membered [1.3.2]-dithiazolium ring in **1**, which is fused with a benzene ring in the [4.5] position, assumes a flat twist conformation with a twofold axis bisecting the C(1) atom

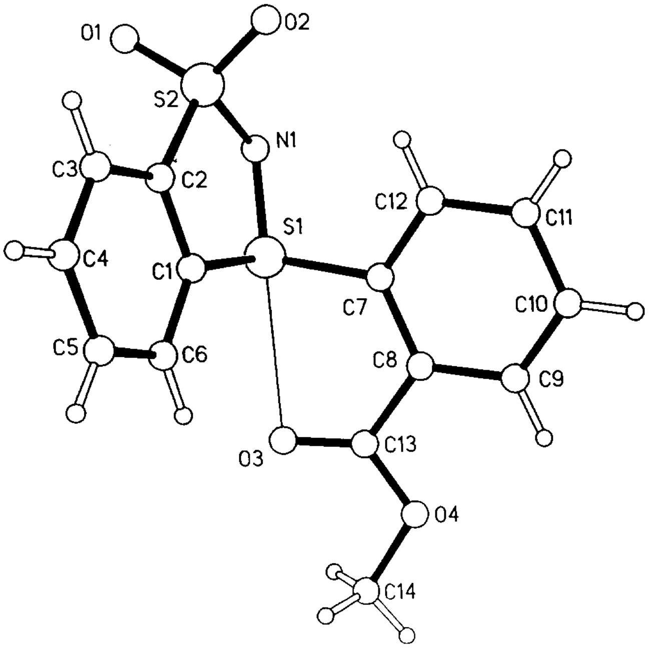

Fig. 2. Solid-state conformation for compound **2** as obtained by X-ray diffraction with atom numbering scheme for non-hydrogen atoms.

Table 3
Relevant geometric parameters with ESDs (in parentheses) for compounds **1**, **2**, and **3**

	1	**2**	**3**[a]
Interatomic distances (r in Å)			
S1 ··· O1	3.803(2)	3.722(2)	3.889(1)
S1 ··· O2	3.487(1)	3.660(2)	2.893(1)
S1 ··· O3	–	2.684(2)	2.710(1)
S1–N1	1.618(2)	1.607(2)	1.632(1)
S2–N1	1.613(2)	1.604(2)	1.609(1)
S2–O1	1.440(2)	1.435(2)	1.434(1)
S2–O2	1.436(2)	1.435(2)	1.443(2)
S1–C1	1.802(3)	1.802(2)	1.790(2)[b]
S2–C2	1.754(3)	1.768(2)	1.767(1)
C1–C2	1.388(3)	1.376(3)	1.378(2)
S1–C7	1.801(4)	1.825(2)	1.812(1)
C7–C8	1.381(3)	1.399(3)	1.400(1)
C8–C13	–	4.492(3)	1.487(2)
C13–O3	–	1.197(3)	1.197(1)
C13–O4	–	1.331(3)	1.321(1)
C14–O4	–	1.450(3)	1.440(2)
Angles (Θ in deg)			
N1–S1 ··· O3	–	170.8(1)	174.6(1)
C1–S1 ··· O3	–	88.9(1)	85.1(1)
C7–S1 ··· O3	–	75.9(1)	75.5(1)
C1–S1–C7	100.4(2)	99.2(2)	99.0(1)
S1–C1–C2	110.0(3)	110.9(3)	–
C1–C2–S2	113.3(4)	113.9(3)	120.4(1)
C2–S2–N1	99.4(2)	98.8(2)	107.4(1)
C2–S2–O13	112.0(2)	109.9(2)	106.7(1)
C2–S2–O2	106.5(2)	109.1(2)	106.8(1)
O1–S2–O2	115.4(2)	114.6(2)	117.2(1)
O1–S2–N1	108.8(2)	109.5(2)	106.7(1)
O2–S2–N1	113.5(2)	113.7(2)	111.7(1)
S1–N1–S2	113.8(2)	116.8(2)	112.1(1)
N1–S1–C1	99.7(2)	99.0(2)	100.1(1)
N1–S1–C7	109.8(2)	107.3(2)	104.8(1)
S1–C7–C8	116.8(4)	120.4(3)	122.0(1)
C7–C8–C13	–	119.6(3)	120.4(2)
C8–C13–O3	–	123.2(4)	123.1(2)
C8–C13–O4	–	112.2(3)	113.2(2)
O3–C13–O4	–	124.5(4)	123.7(2)
C13–O4–C14	–	115.8(3)	116.0(2)
Torsion angles (ϕ in deg)			
"Sulfimide ring"			
ϕ_1 (S1–C1–C2–S2)	-6.4(2)	0.8(1)	–
ϕ_2 (C1–C2–S2–N1)	15.9(3)	3.7(3)	-81.7(2)
ϕ'_2 (C1–C2–S2–O1)	130.8(4)	118.3(4)	164.3(2)
ϕ''_2 (C1–C2–S2–O2)	-102.4(4)	-115.3(4)	38.2(2)
ϕ_3 (S1–N1–S2–C2)	-20.0(2)	-7.5(2)	81.3(1)
ϕ'_3 (S1–N1–S2–O1)	-137.3(2)	-122.4(2)	-164.7(1)
ϕ''_3 (S1–N1–S2–O2)	92.7(2)	107.9(2)	-35.5(1)
ϕ_4 (C1–S1–N1–S2)	16.9(2)	7.9(2)	-150.9(1)
ϕ'_4 (C7–S1–N1–S2)	-87.9(2)	-94.7(2)	106.9(1)
ϕ_5 (C2–C1–S1–N1)	-5.8(3)	-5.0(3)	–

Table 3
Continued

	1	2	3[a]
Aromatic ring position			
ϕ'_5 (C6–C1–S1–C7)	−74.3(3)	−76.7	–
ϕ_6 (C1–S1–C7–C8)	86.2(4)	98.4(3)	86.3(1)
ϕ'_6 (N1–S1–C7–C12)	6.6(4)	14.7(3)	6.8(1)
"Close contact ring"			
ϕ_7 (S1–C7–C8–C13)	–	−8.5(3)	−2.8(2)
ϕ_8 (C7–C8–C13–O3)	–	−10.9(5)	−3.4(3)
ϕ_9 (C8–C13–O3···S1)	–	16.4(2)	5.1(1)
ϕ_{10} (C13–O3···S1–C7)	–	−15.8(3)	−4.9(2)
ϕ_{11} (O3···S1–C7–C8)	–	11.8(2)	3.8(1)

[a] Geometry data for **3** (corresponding to those in **1** and **2**) were computed by using data in ref. [3].
[b] S(IV)–Csp^3 bond distance.

($Q = 0.205(4)$ Å and $\phi = 128(1)°$, according to ref. 12). The endocyclic torsion angles ϕ_1–ϕ_5 are −6°, 16°, −20°, 17°, and −6°. In contrast, the corresponding hetero ring in **2** exhibits a rather flattened envelope conformation ($Q = 0.081(3)$ Å) with the N(1) atom slightly out of the least squares plane ($\Delta = 0.122(2)$ Å of the other four atoms). Here the endocyclic torsion angles ϕ_1–ϕ_5 take up the values ~ 0°, 4°, −7°, 8°, and −5°.

Surprisingly, the S(IV)=N and S(VI)–N bond lengths (1.61–1.62 and 1.60–1.61 Å) in both cyclic sufilimines are almost identical, meaning that the former are somewhat shorter while the latter are somewhat longer than the corresponding values published in the literature [3,13] for acyclic sulfilimines (1.63–1.64 and 1.59–1.60 Å, respectively). On the other hand, the r(S=O) = 1.43–1.44 Å values agree well with those obtained for acyclic analogues [3,13]. In compounds **1** and **2** there are no noticeable differences in S(VI)=O1 and S(VI)=O2 bond distances. This may be due to the lack of conjugation of either S=O bond with the S(VI)-aryl ring or with the S(IV)=N–S(VI) moiety, as will be discussed later in detail. The S–C$_{ar}$ bond lengths practically correspond to the values known from the literature [3,13]: the S(IV)–C$_{ar}$ bonds proved to be longer (1.80–1.82 Å) than the S(VI)–C$_{ar}$ bonds (1.75 Å).

The bond angles characteristic of sulfilimines are not affected significantly by the cyclic structure in **1** and **2**. Both S(IV) and S(VI) atoms preserve the usual pyramidal/tetrahedral configuration. Only the endocyclic ϑ(CSN) bond angles are somewhat smaller than in other cases (99–100° instead of 100–107°). On the other hand, the ϑ(C$_{ar}$C$_{ar}$S) bond angles suffer significant distortion owing to the rigidity of the five-membered dithiazolium ring (110–114° instead of 120°).

4.2. Hetero ring with S···O close contact

As is expected, the replacement of an *ortho*-hydrogen in the phenyl ring of **1** with a methoxycarbonyl group results in a 1,5-type sulfur(IV)-oxygen non-bonded interaction in **2**. Fig. 2 and ϕ_7–ϕ_{11} torsion angles in Table 3 show that a nearly planar hetero ring is formed by S(IV)···O close contact (2.68 Å). Here the N=S(IV)···O moiety is almost linear ($\vartheta = 171°$) and the C$_{ar}$–S(IV)···O angles are nearly rectangular ($\vartheta = 89$ and 76°), both pointing to a sulfurane-like configuration about the S(IV) atom with the N=S(IV)···O distances 1.61 + 2.68 = 4.29 Å. The feature is similar to the case of the acyclic sulfilimine **3** [3] where the linear ($\vartheta = 175°$) N=S(IV)···O sequence is 1.63 + 2.71 = 4.34 Å long. Except for the two sulfilimines **2** and **3**, only three aromatic acylaminosulfonium salts are known [14] in which 1,5-type sulfur(IV)–oxygen non-bonded interaction involves nitrogen as counteratom. In these sulfonium compounds the N–S$^+$···O moiety is nearly linear ($\vartheta = 157$–165°) and

4.12–4.46 Å long with r(S–N) = 1.67–1.69 Å and r(S $\cdots$ O) = 2.45–2.79 Å distances. All compounds discussed above exhibit S $\cdots$ O distances that are unfavourably long to allow the formation of an effective S–O hypervalent bond. By comparing the bond distances, the compounds containing an N=S $\cdots$ O or N–S $\cdots$ O moiety can be well differentiated from "mixed" spirosulfuranes in which the nitrogen and oxygen hetero atoms are in axial positions. In the latter case the linear (174–179°) N–S–O sequence is shorter (3.87–4.17 Å), exhibiting a somewhat longer r(SN) distance (1.71–1.74 Å) and a considerably shorter r(SO) distance (2.13–2.37 Å) as is shown in ref. [14b].

In the acyclic sulfilimine **3** the S(IV), N, S(VI) atoms, and one of the sulfonyl-O atoms are not far from lying in a common plane ($\varphi_3'' = -36°$), which leads to a sulfur–oxygen close contact of 1,4-type with a fairly short S(IV) $\cdots$ O2 distance (2.89 Å). This type of interaction is, however, hindered by the cyclic dithiazolium structure of both **1** and **2**. Consequently, the φ_3'' torsion angles are near to 90° and the long S(IV) $\cdots$ O2 distances (3.49 and 3.66 Å) point to the lack of close contact.

4.3. *Aromatic ring positions*

The two aromatic rings in both cyclic sulfilimines **1** and **2** assume "butterfly" conformation about the sulfur(IV) atom (see refs. [3] and [16]), i.e. they are nearly perpendicular to the S(IV)–N–S(VI) plane ($\varphi_5' = -74°$ and $-77°$, $\varphi_6 = 86°$ and 98° for **1** and **2**, respectively. This conformation allows the S(IV)=N bond to lie nearly in a common plane with the "free" aromatic ring ($\varphi_6' = 7°$ for **1**, and 15° for **2**), which is required for the extension of conjugation. The corresponding data indicate that a similar arrangement occurs in the S(IV)-monoaryl moiety of the acyclic sulfilimine **3** ($\varphi_6 = 86°$ and $\varphi_6' = 7°$). Here it should be mentioned that the butterfly conformation of the two S(IV)–aryl rings was observed only in diphenyl sulfoxide [15], while *S*, *S*-diphenyl-*N*-tosyl-sulfilimine [13a], like sterically hindered sulfoxides [16], exhibits a "twist" conformation with $\varphi = 57°$ instead of 90°.

The torsion angle φ [$\mathrm{C_{ar}}$–$\mathrm{C_{ar}}$–S(VI)–N] in acyclic sulfilimines is near to 90° indicating that the S(VI)–aryl ring is perpendicular to the $\mathrm{C_{ar}}$–S(VI)–N plane ($\varphi_2 = -82°$ in **3**). Because the torsion angle φ[$\mathrm{C_{ar}}$–S(VI)–N–S(IV)] is also almost 90° ($\varphi_3 = 81°$ in **3**) the conformation of the aryl–S(VI)$\mathrm{O_2}$–N–S(IV) moiety corresponds to case II conjugation according to Koch and Moffitt (see Table 5 and Fig. 3 in ref. [13a]). As shown by the torsion angles $\varphi_2' = 164°$ and $\varphi_2'' = 38°$ for the $\mathrm{C_{ar}}$–$\mathrm{C_{ar}}$–S(VI)–O1/O2 part as well as by $\varphi_3' = -165°$ and $\varphi_3'' = -35°$ for the S(IV)–N–S(VI)–O1/O2 part in **3**, the S(VI)=O bonds in this arrangement lie nearly in the plane of both the S(VI)–aryl ring and S(VI)–N–S(IV) moiety, which is a prerequisite for conjugation. The slight elongation of one of the S(VI)=O bonds, 1.443(2) Å instead of 1.434(1) Å, may be attributed to the difference in torsion angles involving O1 and O2 atoms.

The conformation discussed above is sterically inhibited in cyclic sulfilimines, e.g. in **1** and **2**. Here the S(VI)–aryl ring is almost coplanar with the $\mathrm{C_{ar}}$–S(VI)–N moiety ($\varphi_2 = 16°$ for **1**, and 4° for **2**), and the $\mathrm{C_{ar}}$–S(VI)–N–S(IV) part is practically synperiplanar ($\varphi_3 = -20°$ for **1**, and $-7°$ for **2**). Thus the conformation of the aryl–S(VI)$\mathrm{O_2}$–N–S(IV) moiety corresponds to the case I of conjugation according to Koch and Moffitt (see Fig. 4a in ref. [13a]). In this arrangement both the S(VI)=O1 and S(VI)=O2 bonds are far from being coplanar either with the S–aryl ring ($\varphi_2' = 131°$, $\varphi_2'' = -102°$ for **1** and $\varphi_2' = 118°$, $\varphi_2'' = -115°$ for **2**) or with the S(VI)–N–S(IV) moiety ($\varphi_3' = -137°$, $\varphi_3'' = 93°$ for **1**, and $\varphi_3' = -122°$, $\varphi_3'' = 108°$ for **2**). In this case there is no difference in the S(VI)=O1 and S(VI)=O2 bond lengths or it is negligible.

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