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Spiro-λ^4-sulfanes with intramolecular sulfur–oxygen interactions: Syntheses and molecular structures

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Abstract

Three novel *N*-acetylated spiro-λ^4-sulfanes with five-membered spirorings (fused with aromatic rings) and with two N heteroatoms (in (**1**)) or with N and O heteroatoms (in (**2**) and (**3**)) in axial positions have been prepared and their molecular structures determined by X-ray diffraction. The molecular structures of compounds (**1–3**) show trigonal bipyramidal geometry about the central sulfur atom. The rather long axial S–N bonds (1.93 Å) in the symmetric spiro-λ^4-sulfane (**1**) exhibit the usual hypervalent character, whereas the S–N (1.73 and 1.80 Å) and S–O (2.23 and 2.07 Å) bond lengths in the unsymmetric spiro-λ^4-sulfanes (**2**) and (**3**) correspond to elongated covalent S–N bonds and highly polarized S–O hypervalent bonds, respectively. Each structure exhibits usual S–C_{ar} bond lengths (1.79–1.81 Å). The axial N-S-N/O and the equatorial C_{ar}-S-C_{ar} angles lie in the intervals 173–179° and 98–103°, respectively. The conformations of (**1–3**) including the single-*cis*–single-*trans* isomerism of the endocyclic and exocyclic amide parts, the shape of the spirorings, and the relative positions of the equatorial aromatic rings are discussed in detail. In (**1–3**) the exocyclic carbonyl-oxygen approaches the central sulfur atom by 2.90, 2.73 and 2.71 Å, respectively, leading to an effective intramolecular sulfur–oxygen interaction of 1,4-type. The S···O close contacts, however, do not alter appreciably the trigonal bipyramidal geometry about the central sulfur atom. © 1997 Elsevier Science B.V.

Keywords: Hypervalent bonds; Spiro-λ^4-sulfanes; Sulfur–oxygen interaction; X-ray diffraction

1. Introduction

In continuation of our preceding studies on spiro-λ^4-sulfanes (earlier spirosulfuranes) substituted symmetrically or unsymmetrically at axial positions [1–3], we now report on the syntheses and molecular structures of the spiro-λ^4-sulfanes (**1–3**) with intramolecular sulfur–oxygen interaction of 1,4-type [4].

Stable spiro-λ^4-sulfanes are excellent models for studying hypervalent bonding systems about the sulfur atom. The comparison of compound (**4**), the first known representative of symmetric spiro-λ^4-sulfanes [5], with its aza-analogue (**5**) [6] reveals that the S–X hypervalent bonds in a symmetric axial X–S–X moiety (X=O or N) are ''balanced'' and, as in the case of S–X covalent single bonds, they are controlled by the nature of the axial heteroatoms, as shown by the bond length data *r*[S–O(acyloxy)] = 1.84 Å in (**4**)

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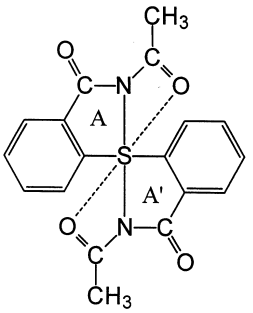

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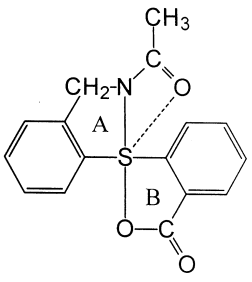

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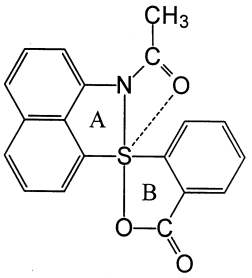

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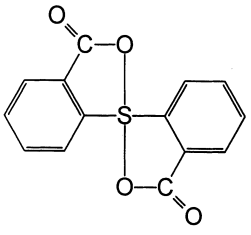
and r[S–N(acylamino)] = 1.90 Å in (**5**) (cf. the sum of the covalent radii, S–O = 1.70 Å and S–N = 1.74 Å in Ref. [7]).



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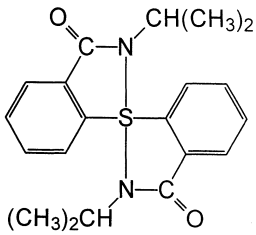

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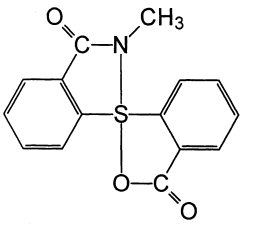
On the other hand, in unsymmetric spiro-λ^4-sulfanes with an axial X–S–Y moiety the bond strengths reflected by the corresponding bond lengths are ''disproportionated''. The S–X bond with a less electronegative X heteroatom is practically as strong as a covalent single bond, as can be seen, for example, from r[S–N(acylamino)] = 1.73 Å in (**6**) [2]. In contrast, the S–Y hypervalent bond with a more electronegative heteroatom is dramatically polarized: in the same compound r[S–O(acyloxy)] = 2.13 Å.



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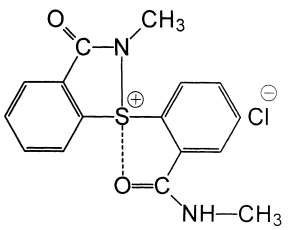

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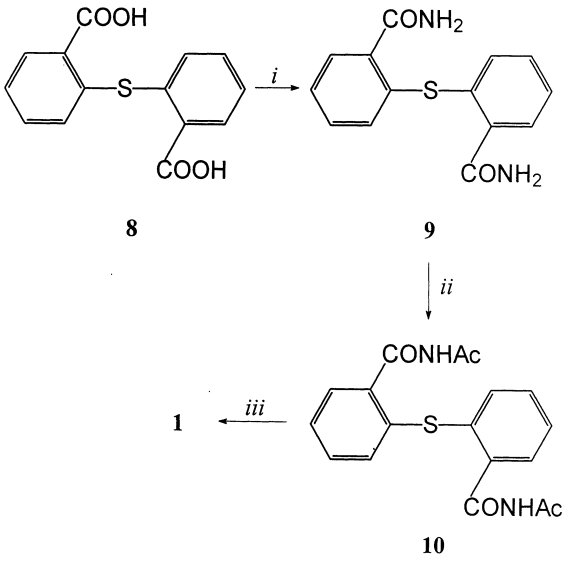
Nevertheless, the polarized (weak) hypervalent bond can be well differentiated from an effective S···O close contact which may be regarded as a ''premature'' hypervalent bond (see Ref. [8]). In the acylaminosulfonium salt (**7**), for example, which is stabilized by an intramolecular S···O(carbamoyl) close contact, a significantly longer r(S···O) = 2.37 Å interatomic distance was determined [2].

By studying the molecular structures of spiro-λ^4-sulfanes (**1–3**) the following questions are to be answered: (i) how the hypervalent S–N bonds in symmetric spiro-λ^4-sulfanes are affected by an exocyclic *N*-alkyl → *N*-acyl change, i.e. by an increase of the electronegativity of the axial nitrogen atoms; (ii) how the N–S–O bonding system in unsymmetric spiro-λ^4-sulfanes is affected by an (*endo*-carbonyl)–(*exo*-methyl) → (*endo*-methylene)–(*exo*-carbonyl) change in the spirocyclic ring system; (iii) whether or not the weakened axial S–O hypervalent bond in unsymmetric spiro-λ^4-sulfanes is altered by an increase of the axial S–N bond length associated with steric constraint; (iv) whether or not an exocyclic *N*-alkyl → *N*-acyl change results in the formation of an intramolecular S···O close contact, and in the former case how the usual trigonal bipyramidal geometry of the spiro-λ^4-sulfanes is affected by the coordination of nonbonded oxygen atom(s) to the central sulfur atom.

1.1. Model compounds

In the synthesis of spiro-λ^4-sulfane (**1**) (Scheme 1),

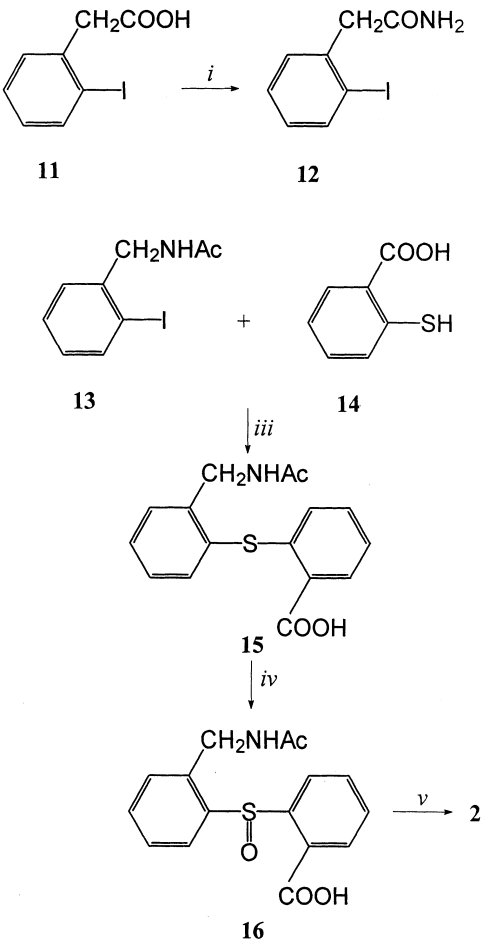


Scheme 1. Synthesis of compound (**1**). Reagents and conditions: (i) $SOCl_2$, reflux, 2 h, then aq. NH_3; (ii) Ac_2O, drop of conc. H_2SO_4, 140 °C, 3 min; (iii) $TsNCl_2$, pyridine, 20 °C, 12 h.

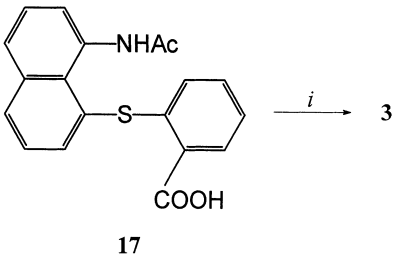
2,2′-thiodibenzoic acid [9] (**8**) was first converted into 2,2′-thiodibenzamide (**9**) through the corresponding acid chloride (path i). The diamide (**9**) obtained was acetylated with AC_2O to (**10**) (path ii), which was then oxidized with dichloramine-T ($TsNCl_2$) under anhydrous conditions to give (**1**) (path iii).

The synthesis of spiro-λ^4-sulfane (**2**) (Scheme 2) started from (2-iodophenyl)acetic acid [10] (**11**) which was treated with $SOCl_2$, then with NH_3 to give (2-iodophenyl)acetamide (**12**) (path i). From amide (**12**) the 2-iodo derivative of *N*-acetylbenzylamine (**13**) was obtained by Hofmann rearrangement followed by *N*-acetylation with AC_2O (path ii). For the preparation of sulfide (**15**) thiosalicylic acid (**14**) was coupled with (**13**) (path iii). The treatment of (**15**) with phenyltrimethylammonium tribromide (PTAB) resulted in sulfoxide (**16**) (path iv), which was dehydrated with AC_2O to yield spiro-λ^4-sulfane (**2**) (path v).

Spiro-λ^4-sulfane (**3**) was prepared from sulfide (**17**) [11] by using dichloramine-T as oxidizing agent (Scheme 3; path i).



Scheme 2. Synthesis of compound (**2**). Reagents and conditions: (i) $SOCl_2$, reflux, 2 h, then aq. NH_3; (ii) aq. NaOBr and NaOH, 80 °C, 2 min, then AcOH-Ac_2O, reflux, 5 min; (iii) Cu_2O, pyridine, reflux, 2 h; (iv) PTAB, pyridine-water, 20 °C, 1 h; (v) Ac_2O, pyridine, 100 °C, then cooling to 20 °C.



Scheme 3. Synthesis of compound (**3**). Reagents and conditions: (i) $TsNCl_2$, pyridine, 0 °C, 12 h.

2. Experimental details

2.1. Materials

Melting points were determined on a Boetius micro melting point apparatus. IR spectra were taken on a Specord IR 75 (Zeiss, Jena) spectrophotometer. Microanalyses were carried out in the microanalytical laboratory of this department by Dr. H. Medzihradszky-Schweiger and co-workers.

Solvents were purified and dried by the usual methods. The evaporations were carried out under reduced pressure. Products obtained from reaction mixtures or by crystallization were dried in vacuo over P_2O_5 or KOH pellets, depending on the solvent used.

2.2. 2,2′-diacetyl-1,1′-spirobi[3H-2,1-benzazathiole] (**1**)

2.2.1. Path (i) in Scheme 1

To 2,2′-thiodibenzoic acid [9] (**8**; 32.1 g, 0.117 mol) was added 53 ml (0.73 mol) of thionyl chloride and the reaction mixture was refluxed for 2 h, then the excess of thionyl chloride was removed by evaporation. The crude acid chloride residue was dissolved in dry dioxane (150 ml), and 120 ml of aqueous NH_3 was added dropwise to the stirred solution at room

Table 1
Crystal and relevant X-ray data for compounds (**1–3**)

Compound	(**1**)	(**2**)	(**3**)
Formula	$C_{18}H_{14}N_2O_4S$	$C_{16}H_{13}NO_3S$	$C_{19}H_{13}NO_3S$
MW	354.37	299.35	335.38
Crystal size (mm)	$0.15\times0.35\times0.35$	$0.13\times0.16\times0.30$	$0.18\times0.20\times0.25$
Crystal system	tetragonal	monoclinic	triclinic
Space group	$I4_3$	$P2_1/c$	$P-1$
a (Å)	12.596(1)	7.872(1)	7.665(1)
b (Å)	12.596(1)	13.340(1)	8.031(1)
c (Å)	10.278(1)	13.463(1)	12.448(1)
α (°)	90	90	105.1(1)
β (°)	90	97.95(1)	95.17(1)
γ (°)	90	90	94.71(1)
V (Å^3)	1630.7(2)	1400.2(4)	732.3(3)
Z	4	4	2
D_{calc} (g cm^{-3})	1.44	1.42	1.52
F (000)	736	624	348
Temperature (K)	293(2)	295(2)	296(2)
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan rate (deg/min)	1–20	1–20	1–20
X-ray radiation	Cu Kα	Cu Kα	Mo Kα
λ (Å)	1.54184	1.54184	0.71073
μ (mm^{-1})	2.00	2.09	0.23
θ range (°)	1.5–75.0	1.5–75.0	1.5–30.0
Total reflections	888	2881	4265
Nonzero reflections	886	2481	3054
Refinement on	F^2	F	F
Parameters refined	117	191	269
σ level	2.0	3.0	3.0
$R=\Sigma\Delta F/\Sigma F_O$	0.037	0.042	0.034
$R_w=\Sigma w(\Delta F^2)/\Sigma\lvert F_O^2\rvert$	0.093	0.077	0.037
R indices (all data)	0.038	0.052	0.073
$S=\Sigma(w\lVert F_O\rvert-\lvert F_C\rVert^2)/(N_O-P)^{1/2}$	1.20	2.73	0.46
Max. (Δ/σ)	0.001	0.068	0.078
$\Delta\rho_{max}$ (e.Å^{-3})	0.23	|0.23|	|0.26|
$\Delta\rho_{min}$ (e.Å^{-3})	–0.23		

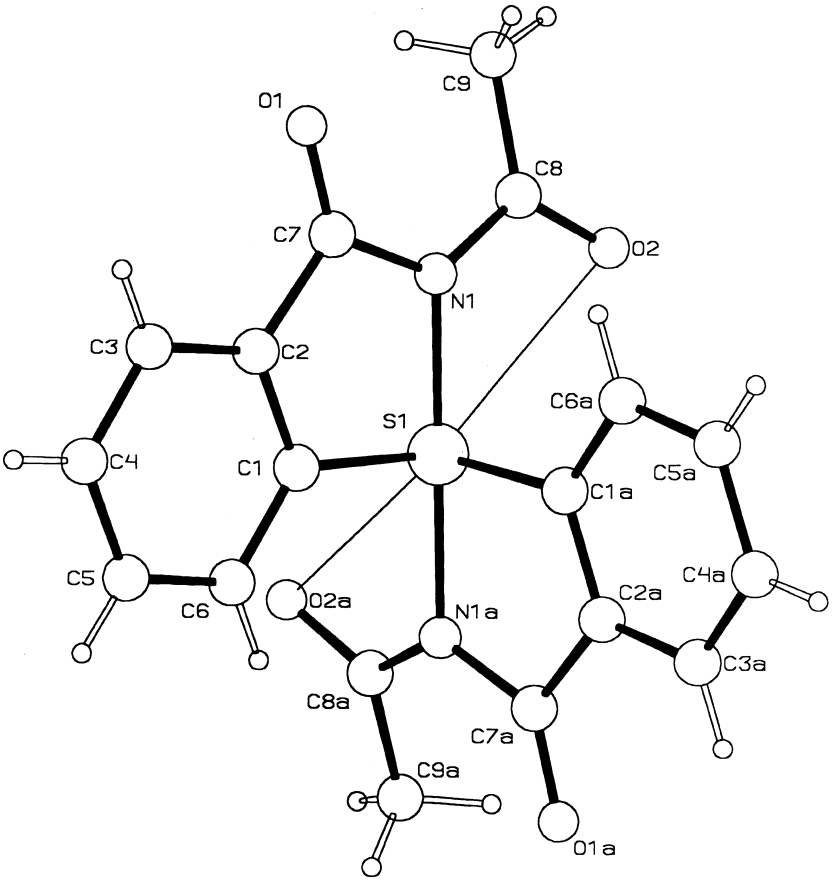


Fig. 1. Perspective view of spiro-λ^4-sulfane (**1**) with numbering scheme for nonhydrogen atoms.

temperature. After standing overnight the solvent was removed in vacuo, the residue was triturated with water (100 ml), filtered and dried to yield 2,2′-thiodibenzamide (**9**; 29.7 g, 93%); after crystallization from MeOH, m.p. 209–210 °C (207–209 °C in Ref. [12]).

2.2.2. Path (ii) in Scheme 1

The mixture of diamide (**9**) (12 g, 0.044 mol), Ac_2O (33 ml, 0.352 mol) and 0.2 ml of concentrated H_2SO_4 was heated in an oil bath at 140 °C for 3 minutes then poured into crushed ice (250 g). The precipitate was filtered off, washed with water and dried to give *N*,*N*′-diacetyl-2,2′-thiodibenzamide (**10**; 14.4 g, 92%), m.p. 190–194 °C (after crystallization from AcOH-H_2O). IR (KBr): 3255s, 3170m (NH), 1730vs, 1695s (C=O) cm^{-1}. Elemental analysis: calculated for $C_{18}H_{16}N_2O_4S$ (356.4), C 60.66, H 4.52, N 7.86, O 17.96, S 9.00%; found, C 60.3, H 4.4, N 7.7, O 17.9, S 8.7%.

2.2.3. Path (iii) in Scheme 1

To a solution of (**10**) (1.05 g, 3 mmol) in dry pyridine (10 ml) dichloramine-T ($TsNCl_2$; 0.39 g, 1.6 mmol) was added and the reaction mixture was allowed to stand at room temperature overnight. The crystals of spiro-λ^4-sulfane (**1**) were filtered off, washed with dry pyridine, acetone and ether, then dried. Yield: 0.33 g (31%), m.p. 222–228 °C. IR (KBr): 1690vs, 1660vs (C=O) cm^{-1}. Elemental analysis: calculated for $C_{18}H_{14}N_2O_4S$ (354.4), C 61.01, H 3.98, N 7.90, O 18.07, S 9.05%; found, C 60.4, H 4.0, N 7.9, O 17.9, S 9.0%.

Table 2
Fractional atomic coordinates and mean equivalent isotropic displacement parameters U_{eq} (Å^2) for nonhydrogen atoms in compounds (**1–3**) with ESDs in parentheses. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Compound (**1**)				
S(1)	0	0	0.0000(1)	0.029(1)
O(1)	–0.1385(2)	–0.2765(2)	–0.0854(3)	0.045(1)
O(2)	0.1142(2)	–0.1653(2)	0.1376(3)	0.056(1)
N(1)	–0.0203(2)	–0.1515(2)	–0.0046(3)	0.032(1)
C(1)	–0.1112(2)	0.0058(2)	–0.1111(3)	0.032(1)
C(2)	–0.1554(2)	–0.0918(2)	–0.1391(3)	0.035(1)
C(3)	–0.2401(3)	–0.1004(3)	–0.2252(4)	0.045(1)
C(4)	–0.2794(3)	–0.0087(3)	–0.2822(5)	0.054(1)
C(5)	–0.2347(3)	0.0893(3)	–0.2533(5)	0.051(1)
C(6)	–0.1507(3)	0.0979(3)	–0.1674(4)	0.040(1)
C(7)	–0.1070(2)	–0.1864(2)	–0.0745(3)	0.032(1)
C(8)	0.0365(3)	–0.2081(3)	0.0891(3)	0.037(1)
C(9)	0.0004(3)	–0.3157(3)	0.1260(4)	0.046(1)
Compound (**2**)				
S(1)	0.0783(1)	–0.1870(1)	–0.0971(1)	0.037(2)
O(1)	0.2985(3)	–0.4169(1)	0.0820(1)	0.075(1)
O(2)	0.1429(2)	–0.2802(1)	0.0406(1)	0.053(1)
O(3)	–0.1217(2)	–0.2463(2)	–0.2691(2)	0.065(1)
N(1)	0.0265(2)	–0.1137(1)	–0.2027(1)	0.042(1)
C(1)	0.1762(3)	–0.0791(2)	–0.0335(2)	0.038(1)
C(2)	0.1770(3)	0.0030(2)	–0.0955(2)	0.041(1)
C(3)	0.2504(4)	0.0919(2)	–0.0564(2)	0.055(1)
C(4)	0.3231(3)	0.0959(2)	0.0421(2)	0.058(1)
C(5)	0.3205(4)	0.0131(2)	0.1035(2)	0.057(1)
C(6)	0.2456(3)	–0.0763(2)	0.0674(2)	0.048(1)
C(7)	0.0944(4)	–0.0119(2)	–0.2011(2)	0.050(1)
C(8)	0.2636(3)	–0.2517(2)	–0.1318(2)	0.036(1)
C(9)	0.3351(3)	–0.3258(2)	–0.0665(2)	0.040(1)
C(10)	0.4784(3)	–0.3767(2)	–0.0894(2)	0.049(1)
C(11)	0.5502(3)	–0.3508(2)	–0.1748(2)	0.057(1)
C(12)	0.4761(3)	–0.2779(2)	–0.2380(2)	0.051(1)
C(13)	0.3301(3)	–0.2274(2)	–0.2186(2)	0.041(1)
C(14)	0.2540(3)	–0.3451(2)	0.0267(2)	0.047(1)
C(15)	–0.0841(3)	–0.1583(2)	–0.2780(2)	0.051(1)
C(16)	–0.1523(4)	–0.0947(3)	–0.3652(2)	0.074(1)
Compound (**3**)				
S(1)	0.2229(1)	0.2718(1)	0.2475(1)	0.0314(1)
O(1)	0.5082(3)	0.7407(2)	0.3230(1)	0.0633(8)
O(2)	0.2867(2)	0.5300(2)	0.2552(1)	0.0471(6)
O(3)	0.1005(2)	0.1381(2)	0.4081(1)	0.0467(6)
N(1)	0.1665(2)	0.0441(2)	0.2335(1)	0.0311(5)
C(1)	0.2695(2)	0.2154(2)	0.1046(1)	0.0319(6)
C(2)	0.3291(3)	0.3242(2)	0.0446(2)	0.0412(7)
C(3)	0.3564(3)	0.2506(3)	–0.0673(2)	0.0476(8)
C(4)	0.3226(3)	0.0770(3)	–0.1165(2)	0.0448(8)
C(5)	0.2178(3)	–0.2189(3)	–0.0993(2)	0.0429(8)
C(6)	0.1625(3)	–0.3139(3)	–0.0303(2)	0.0447(8)
C(7)	0.1434(3)	–0.2407(2)	0.0836(2)	0.0394(7)
C(8)	0.1772(2)	–0.0647(2)	0.1257(1)	0.0298(6)

Table 2 Continued

Atom	x/a	y/b	z/c	U_{eq}
C(9)	0.2349(2)	0.0360(2)	0.0561(1)	0.0295(6)
C(10)	0.2587(2)	–0.0374(2)	–0.0566(1)	0.0355(7)
C(11)	0.4376(2)	0.2952(2)	0.3263(1)	0.0288(6)
C(12)	0.5292(2)	0.4597(2)	0.3505(1)	0.0332(6)
C(13)	0.6927(3)	0.4924(3)	0.4127(2)	0.0416(8)
C(14)	0.7629(3)	0.3611(3)	0.4495(2)	0.0452(8)
C(15)	0.6703(3)	0.1984(2)	0.4250(2)	0.0407(7)
C(16)	0.5053(2)	0.1635(2)	0.3631(1)	0.0323(6)
C(17)	0.4409(3)	0.5924(2)	0.3083(2)	0.0414(7)
C(18)	0.0919(2)	0.0159(2)	0.3252(1)	0.0347(6)
C(19)	0.0086(3)	–0.1605(3)	0.3208(2)	0.0453(8)

*2.3. Spiro[3H-2,1-benzoxathiole-3′-one-1,1′-3H-2-acetyl-2,1-benzazathiole] (***2**)

2.3.1. Path (i) in Scheme 2

The mixture of (2-iodophenyl)acetic acid [10] (**11**; 65.5 g, 0.25 mol) and thionyl chloride (36 ml, 0.5 mol) was refluxed for 2 h, then the excess of thionyl chloride was removed in vacuo. The crude acid chloride was dissolved in dioxane (50 ml) and the solution was added dropwise to aqueous NH_3 (150 ml) at room temperature. After standing overnight the reaction mixture was evaporated, the residue was triturated with water (100 ml), filtered and dried. The crude (2-iodophenyl)acetamide (**12**) was crystallized from EtOH, yielding 35.2 g (54%) of pure product, m.p. 180–182 °C. IR (KBr): 3480–3250br (NH), 1660vs (C=O) cm^{-1}. Elemental analysis: calculated for C_8H_8INO (261.1), C 36.80, H 3.09, I 48.60, N 5.36, O 6.13%; found, C 36.5, H 3.0, I 48.4, N 5.4, O 6.1%.

2.3.2. Path (ii) in Scheme 2

To a cold (0 °C) solution of NaOH (21 g, 0.52 mol) in 84 ml of water was first added bromine (5.9 ml, 0.11 mol) then amide (**12**) (29.4 g, 0.112 mol) and 15.4 g (0.38 mol) NaOH in 56 ml of water. After vigorous stirring for 15 minutes the reaction mixture was heated to 80 °C for 2 minutes, then the crude 2-iodobenzylamine product was isolated by steam distillation followed by extraction with ether (150 ml). After evaporation the residue was dissolved in the mixture of AcOH (35 ml) and Ac_2O (7 ml) then refluxed for 5 minutes. The solution was poured into cold water (200 ml), the precipitate was filtered off, washed with water and dried to give *N*-(2-iodobenzyl)-acetamide (**13**; 13 g, 42%), m.p. 129–133 °C (134–135 °C in Ref. [13]).

2.3.3. Path (iii) in Scheme 2

A mixture of (**13**) (13 g, 0.047 mol), thiosalicylic acid (**14**; 7.3 g, 0.047 mol) and Cu_2O (3 g, 0.023 mol) in dry pyridine (80 ml) was refluxed under N_2 (2 h) and, after cooling to room temperature, was poured into a mixture of ice (300 g) and concentrated aqueous HCl (150 ml). The precipitate was filtered off, washed with water, then heated with a solution of Na_2CO_3 (5 g) in water (100 ml) at 100 °C (1 h). After filtration the filtrate was cooled and acidified with concentrated aqueous HCl (pH 1) under external ice-water cooling. The solid product was filtered off, washed with water and dried; the crude 2-[2-(acetylaminomethyl)phenylthio]benzoic acid (**15**; 10.4 g, 74%) was crystallized from EtOH, m.p. 182–183 °C. IR (KBr): 3295s (NH), 3360–2100br (OH), 1682vs, 1655vs (C=O) cm^{-1}. Elemental analysis: calculated for $C_{16}H_{15}NO_3S$ (301.4), C 63.76, H 5.02, N 4.65, O 15.93, S 10.64%; found C 63.8, H 5.1, N 5.0, O 16.2, S 10.9%.

2.3.4. Path (iv) in Scheme 2

To a solution of sulfide (**15**) (0.53 g, 1.8 mmol) in 3.5 ml of pyridine and 0.2 ml of water was added phenyltrimethylammonium tribromide (PTAB; 0.66 g, 1.8 mmol). The mixture was stirred at room temperature for 1 h then poured into ice-cold 2N H_2SO_4 (50 ml). After standing overnight (4 °C) the precipitate formed was filtered off, washed with cold water and dried to give 2-[2-(acetylaminomethyl)phenyl-

Table 3
Relevant geometric parameters for compound (**1**) with ESDs in parentheses [a]

Interatomic distances (Å)			
Spiroring	A		A
S(1)···O(2)	2.899(3)	C(7)–N(1)	1.379(4)
S(1)–N(1)	1.926(3)	C(7)–O(1)	1.207(4)
S(1)–C(1)	1.809(3)	C(8)–N(1)	1.396(4)
C(1)–C(2)	1.380(4)	C(8)–C(9)	1.479(5)
C(2)–C(7)	1.494(4)	C(8)–O(2)	1.224(5)
Bond angles (°)			
Spiroring	A	Exocyclic part	A
N(1)-S(1)-N(1a)	177.2(2)	C(8)-N(1)-S(1)	114.9(4)
N(1)-S(1)-C(1)	85.5(2)	C(2)-C(7)-O(1)	125.0(5)
S(1)-C(1)-C(2)	114.1(4)	O(1)-C(7)-N(1)	127.5(5)
C(1)-C(2)-C(7)	116.9(4)	C(7)-N(1)-C(8)	127.1(5)
C(2)-C(7)-N(1)	107.5(4)	N(1)-C(8)-C(9)	119.2(5)
C(7)-N(1)-S(1)	115.7(3)	N(1)-C(8)-O(2)	117.8(5)
N(1)-S(1)-C(1a)	92.7(2)	O(2)-C(8)-C(9)	123.0(6)
C(1)-S(1)-C(1a)	101.7(2)		
S···O close contact	A		A
O(2)···S(1)-N(1)	50.7(2)	O(2)···S(1)-N(1a)	131.1(2)
O(2)···S(1)-C(1)	136.2(2)	O(2)···S(1)-C(1a)	84.0(2)
O(2)···S(1)···O(2a)	121.6(1)	S(1)···O(2)-C(8)	73.8(4)
Torsion angles (°)			
Spiroring	A	Aromatic ring position	A
S(1)-C(1)-C(2)-C(7)	0.5(3)	C(2)-C(1)-S(1)-C(1a)	94.0(3)
C(1)-C(2)-C(7)-N(1)	–3.9(4)	C(2)-C(1)-S(1)-N(1a)	179.9(3)
C(2)-C(7)-N(1)-S(1)	2.1(3)	C(6)-C(1)-S(1)-C(1a)	–85.1(4)
C(7)-N(1)-S(1)-C(1)	–4.7(3)	C(6)-C(1)-S(1)-N(1a)	0.8(4)
N(1)-S(1)-C(1)-C(2)	2.1(3)		
Acylamino part	A		A
C(1)-C(2)-C(7)-O(1)	177.4(5)	C(7)-N(1)-C(8)-C(9)	–3.2(5)
S(1)-N(1)-C(7)-O(1)	–175.9 (7)	C(7)-N(1)-C(8)-O(2)	177.2(6)
C(2)-C(7)-N(1)-C(8)	167.2(6)	S(1)-N(1)-C(8)-C(9)	158.6(7)
O(1)-C(7)-N(1)-C(8)	–14.2(6)	S(1)-N(1)-C(8)-O(2)	–21.0(4)
S···O close contact	A		
N(1)-C(8)-O(2)···S(1)	13.0(3)		
C(8)-O(2)···S(1)-N(1)	–10.7(4)		
O(2)···S(1)-N(1)-C(8)	10.0(3)		

[a] N(1a), O(1a), O(2a) and C(1a)–C(7a) are generated atoms.

sulfinyl]benzoic acid (**16**; 0.48 g, 86%), m.p. 221–223 °C. IR (KBr): 3270s (NH), 1695s, 1615s (C=O), 1715vs (S=O) cm^{-1}. Elemental analysis: calculated for $C_{16}H_{15}NO_4S$ (317.4), C 60.55, H 4.76, N 4.41, O 20.16, S 10.10%; found, C 60.7, H 4.9, N 4.2, O 20.1, S 10.0%.

2.3.5. Path (v) in Scheme 2

To a solution of sulfoxide (**16**) (0.32 g, 1 mmol) in dry pyridine (2 ml) obtained by heating at 100 °C was added Ac_2O (1 ml), and the mixture was allowed to cool to 20 °C. After standing for 12 h, the crystals of spiro-λ^4-sulfane (**2**) were filtered off, washed with

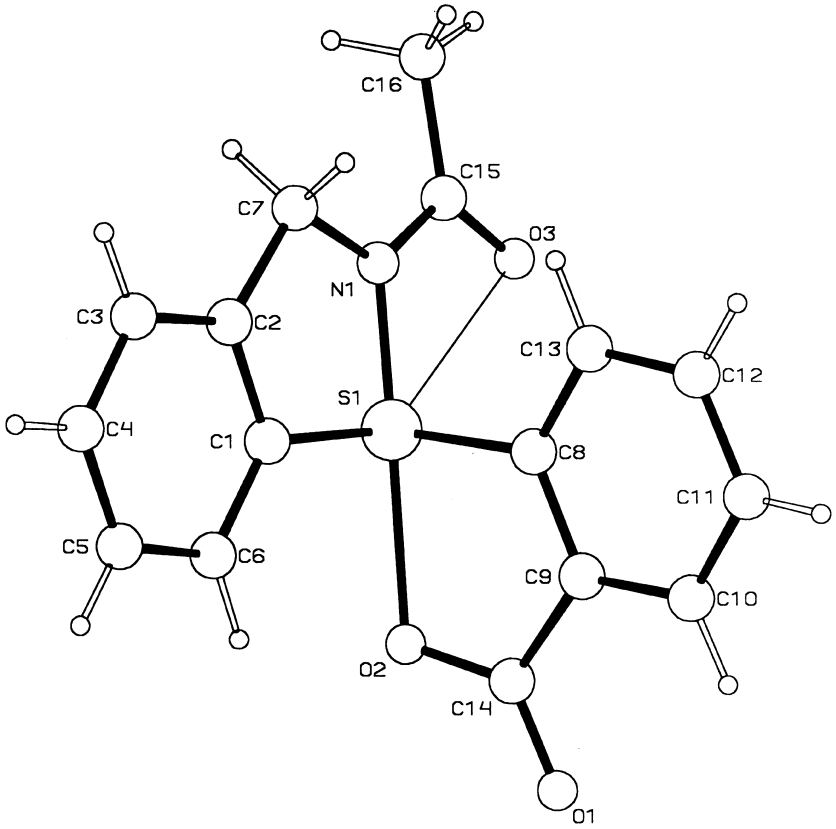


Fig. 2. Perspective view of spiro-λ^4-sulfane (**2**) with numbering scheme for nonhydrogen atoms.

cold dry pyridine, acetone and ether, then dried. Yield: 0.27 g (89%), m.p. 224–235 °C. IR (KBr): 1670vs, 1635vs, 1620vs (C=O) cm^{-1}. Elemental analysis: calculated for $C_{16}H_{13}NO_3S$ (299.3), C 64.21, H 4.38, N 4.68, O 16.04, S 10.71%; found, C 64.0, H 4.3, N 4.9, O 16.4, S 11.0%.

*2.4. 2′-acetyl-[3H-2,1-benzoxathiole]-1,1′-spiro-[2H-naphtho(1,8-c,d)*isothiazole]-3-one (**3**)

2.4.1. Path (i) in Scheme 3

To a solution of 2-(8-acetylamino-1-naphthylthio)-benzoic acid [11] (**17**; 0.17 g, 0.5 mmol) in dry pyridine (0.4 ml) was added dichloramine-T ($TsNCl_2$; 0.062 g, 0.26 mmol) at 0 °C. After standing overnight the crystals were filtered off, washed with pyridine and ether, then dried to give spiro-λ^4-sulfane (**3**) (0.15 g, 90%) m.p. 237–239 °C. IR (KBr): 1653vs (C=O) cm^{-1}. Elemental analysis: calculated for $C_{19}H_{13}NO_3S$ (335.7), C 68.95, H 3.88, N 4.18, O 14.31, S 9.55%; found, C 68.2, H 3.9, N 4.4, O 13.9, S 9.4%.

2.5. Crystal structure determinations

Intensities for compounds (**1**) and (**2**) were recorded on an Enraf Nonius CAD-4 diffractometer with graphite monochromated Cu Kα radiation using ω-2θ scan in the range $1.5 < \theta < 75°$, whereas for compound (**3**) monochromated Mo Kα radiation was applied collecting data in the range $1.5 < \theta < 30°$. For each crystal three standard reflections were monitored in every hour. No decay correction was applied in either case. Cell constants (Table 1) for each crystal were determined by least-squares refinement of diffractometer angles for 25 automatically centred reflections. Data were collected with the Miller indices:

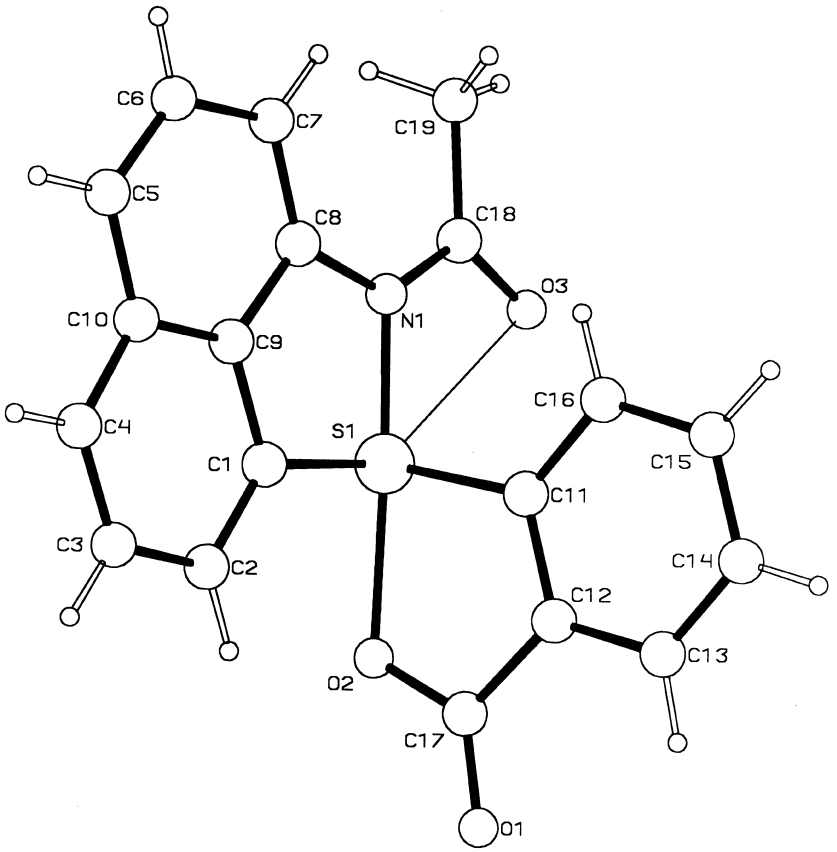


Fig. 3. Perspective view of spiro-λ^4-sulfane (**3**) with numbering scheme for nonhydrogen atoms.

Compound (**1**):

$-15 \le h \le 15,\ 0 \le k \le 15,\ 0 \le l \le 12$

Compound (**2**):

$0 \le h \le 9,\ 0 \le k \le 16,\ -16 \le l \le 16$

Compound (**3**):

$-10 \le h \le 0,\ -11 \le k \le 11,\ -17 \le l \le 17$

Data were corrected for Lorentz and polarization effects. The phase problems were solved by direct methods using SHELX-76 [14] for (**1**) and program MULTAN [15] for (**2**) and (**3**).

For crystals (**1**) and (**2**) empirical absorption corrections [16] were calculated at the end of the isotropic least-squares refinement for the positional parameters of nonhydrogen atoms. Full matrix least-squares refinement minimized $\Sigma w(\Delta F^2)$ with $w = 4F_O^2/\sigma^2(F_O^2)$ using reflections with the criterion $I > 3\sigma$ for (**2**) and (**3**) while for (**1**) $\Sigma w(\Delta F^2)^2$ was minimized for all unique reflections by the program SHELXL 93 [17] with the weighting scheme $1/[\sigma^2(F_O)^2 + (0.0398P)^2 + 1.0802P]$ where $P = (F_O^2 + 2F_C^2)/3$. In each case, the fractional coordinates of the hydrogen atoms were generated from assumed geometries. The hydrogen positions were refined isotropically for (**1**) and (**3**), whereas in the case of (**2**) they were only included in the final structure factor calculations with mean isotropic temperature factors $B_{iH} = B_{iC} + 1$ Å^2 to the corresponding heavy atoms with isotropic displacement parameters. Because (**1**) crystallized with the polar space group $I4_3$ (No. 80) Flack parameter [18] was refined to 0.02(4). Consequently, Fig. 1 depicts the absolute configuration of the crystal specimen mounted on the diffractometer. Scattering factors, including corrections for anomalous dispersion, were taken from standard tables [19]. Calculations for (**1**)

were carried out by the use of SHELXL 93 [17] adapted on a DEC5000 computer, while the calculations for (**2**) and (**3**) were performed on a PDP 11/34 128 kw minicomputer using SDP-plus and local programs.

Fractional coordinates and mean temperature factors (U_{eq}) with ESDs (estimated standard deviations) in parentheses for nonhydrogen atoms in compounds (**1–3**) are listed in Table 2. Because (**1**) has molecular symmetry C_2, coordinates are given in Table 2 only for half of the molecule, and geometric parameters are listed in Table 3 in the same way. Of course, the cross angles (like C_{ar}-S-C_{ar}) as well as the corresponding torsion angles are presented in Table 3.

3. Results and discussion

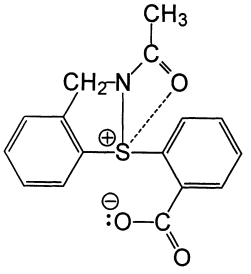
The perspective representations of spiro-λ^4-sulfanes (**1–3**) are shown in Fig. 1, Fig. 2 and Fig. 3, and the relevant geometric parameters are summarized in Table 3, Table 4 and Table 5.

3.1. Sulfur configuration

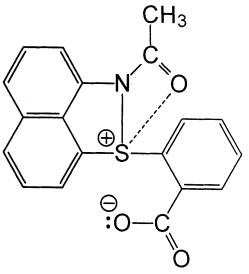
As is known, spiro-λ^4-sulfanes exhibit almost perfect trigonal bipyramidal geometry with identical or different atoms (X and Y = e.g. O or N) in axial positions. The X(axial)-S-Y(axial) bond angles are near 180°, and the X/Y(axial)-S-C(equatorial) bond angles are practically rectangular, independent both of the identity of heteroatoms and of the size of spirorings [1,2,6]. This statement is true for the structures (**1–3**) as well: the N-S-N or N-S-O bond angles are 177°, 179° and 177°, respectively. The endocyclic N-S-C or O-S-C bond angles range from 81° to 89°, whereas the exocyclic analogues are usually wider than 90° (89–99°). The C(equatorial)-S-C(equatorial) bond angles in (**1–3**) ($\vartheta = 102°$, 101° and 103°, respectively) are somewhat smaller than those found, for example, in the analogous compounds (**4–6**) ($\vartheta = 104–107°$).

3.2. Bond lengths about the central sulfur

In the symmetric (diacylamino)spiro-λ^4-sulfane (**1**) with acetyl-substituted nitrogen heteroatoms in axial positions, the axial S–N bonds (1.93 Å) are considerably longer than the sum of the covalent radii of the S and N atoms (1.74 Å [7]). As in other cases, the bond



2A



3A

elongation can be interpreted on the basis of Musher's theory [20] assuming hypervalent three-centre four-electron bonds in the axial array. The slight increase (0.03 Å) in S–N bond lengths of (**1**) related to the analogous bonds in (diacylamino)spiro-λ^4-sulfane (**5**) [6] with alkyl-substituted axial nitrogen atoms may be attributed to the somewhat different electronegativities of nitrogen atoms carrying an exocyclic acetyl or alkyl substituent.

As is expected from the known structure of spiro-λ^4-sulfane (**6**) [2] with different (N and O) heteroatoms in axial positions, the axial S–N interatomic distance in *N*-acetyl-substituted (alkylamino)(acyloxy) spiro-λ^4-sulfane (**2**) corresponds to a slightly elongated S–N covalent bond rather than a usual S–N hypervalent bond (1.73 Å in both (**2**) and (**6**)). On the other hand, the S–O interatomic distances in both compounds (2.13 Å in (**6**) and 2.23 Å in (**2**)) are significantly elongated compared with the usual hypervalent S–O bonds (1.84 Å) found for example in the symmetric (diacyloxy)spiro-λ^4-sulfane (**4**) [1]. Bond elongation points to a remarkably polarized hypervalent S–O bond as shown by the predominant limiting structure (**2A**) (cf. Refs. [2,4,8]).

The disproportion of the axial bond strengths may be ascribed to the different electronegativity of the axial N and O heteroatoms. The r(N–S–O) = 3.96 Å distance characterizing the axial array in (**2**) markedly differs from the analogous r(N–S···O) = 4.06 Å distance observed [2] for the cyclic acylaminosulfonium compound (**7**) which is stabilized by an intramolecular S···O close contact arising from the *ortho*-carbamoyl substituent. The comparison of compounds (**2**) and (**6**) indicates that S–N bond length does not depend on whether the endocyclic methylenamino group is *N*-acetylated (in (**2**)) or the

Table 4
Relevant geometric parameters for compound (**2**) with ESDs in parentheses

Interatomic distances (Å)			
Spirorings	A		B
S(1)···O(3)	2.731(2)	S(1)–O(2)	2.231(2)
S(1)–N(1)	1.727(2)	S(1)–C(8)	1.811(2)
S(1)–C(1)	1.793(2)	C(8)–C(9)	1.390(3)
C(1)–C(2)	1.378(3)	C(9)–C(14)	1.506(3)
C(2)–C(7)	1.493(3)	C(14)–O(2)	1.263(3)
C(7)–N(1)	1.458(3)	C(14)–O(1)	1.234(3)
C(15)–N(1)	1.377(3)		
C(15)–C(16)	1.487(4)		
C(15)–O(3)	1.221(3)		
Bond angles (°)			
Spirorings	A		B
N(1)-S(1)-O(2)	179.1(1)	O(2)-S(1)-C(8)	81.4(1)
N(1)-S(1)-C(1)	88.6(2)	S(1)-C(8)-C(9)	116.5(3)
S(1)-C(1)-C(2)	112.8(3)	C(8)-C(9)-C(14)	117.9(3)
C(1)-C(2)-C(7)	115.7(3)	C(9)-C(14)-O(2)	112.9(3)
C(2)-C(7)-N(1)	104.4(3)	C(14)-O(2)-S(1)	110.0(2)
C(7)-N(1)-S(1)	118.1(2)	O(2)-S(1)-C(1)	91.0(1)
N(1)-S(1)-C(8)	99.4(2)		
C(1)-S(1)-C(8)	101.4(2)		
Exocyclic parts	A		B
C(7)-N(1)-C(15)	127.3(3)	C(9)-C(14)-O(1)	121.1(4)
N(1)-C(15)-C(16)	117.2(4)	O(2)-C(14)-O(1)	126.0(4)
N(1)-C(15)-O(3)	118.7(4)		
O(3)-C(15)-C(16)	124.1(4)		
C(15)-N(1)-S(1)	114.5(3)		
S···O close contact	A		B
O(3)···S(1)-N(1)	54.8(1)	O(3) S(1)-O(2)	125.6(1)
O(3)···S(1)-C(1)	142.8(1)	O(3) S(1)-C(8)	91.9(1)
S(1)···O(3)-C(15)	71.7(2)		
Torsion angles (°)			
Spirorings	A		B
S(1)-C(1)-C(2)-C(7)	1.4(2)	S(1)-C(8)-C(9)-C(14)	– 0.4(2)
C(1)-C(2)-C(7)-N(1)	3.4(3)	C(8)-C(9)-C(14)-O(2)	– 9.5(3)
C(2)-C(7)-N(1)-S(1)	– 7.3(2)	C(9)-C(14)-O(2)-S(1)	12.5(2)
C(7)-N(1)-S(1)-C(1)	7.1(3)	C(14)-O(2)-S(1)-C(8)	– 10.8(3)
N(1)-S(1)-C(1)-C(2)	– 4.6(2)	O(2)-S(1)-C(8)-C(9)	5.4(2)
Aromatic ring positions	A		B
C(2)-C(1)-S(1)-C(8)	94.7(2)	C(9)-C(8)-S(1)-C(1)	94.6(3)
C(2)-C(1)-S(1)-O(2)	176.1(3)	C(9)-C(8)-S(1)-N(1)	– 174.9(3)
C(6)-C(1)-S(1)-C(8)	– 85.0(2)	C(13)-C(8)-S(1)-C(1)	– 84.9(3)
C(6)-C(1)-S(1)-O(2)	– 3.7(3)	C(13)-C(8)-S(1)-N(1)	5.6(3)
Acylamino part	A	Acyloxy part	B
C(2)-C(7)-N(1)-C(15)	169.0(4)	C(8)-C(9)-C(14)-O(1)	171.8(4)
C(7)-N(1)-C(15)-C(16)	– 4.4(4)	S(1)-O(2)-C(14)-O(1)	– 168.8(7)

Table 4 Continued

Interatomic distances (Å)	
C(7)-N(1)-C(15)-O(3)	176.4(4)
S(1)-N(1)-C(15)-C(16)	172.0(5)
S(1)-N(1)-C(15)-O(3)	– 7.2(3)
S···O close contact	A
N(1)-C(15)-O(3)···S(1)	4.4(2)
C(15)-O(3)···S(1)-N(1)	– 3.7(3)
O(3)···S(1)-N(1)-C(15)	3.4(2)

endocyclic carbonylamino group is *N*-methylated (in (**6**)). This phenomenon may be explained by the fact that the electronegativity of the axial nitrogen atoms carrying an acyl, an alkyl and a sulfenyl substituent in both cases is the same.

Formulae show that there is a structural analogy between the *N*-acetyl-substituted (arylamino)(acyloxy) spiro-λ^4-sulfane (**3**) and compound (**2**) with spirocyclic (aralkylamino)(acyloxy) moieties and exocyclic *N*-acetyl group. In the case of (**3**), however, the axial S–N part is connected to the 1,8 (peri) position of a naphthalene ring, which causes considerable strain in the five-membered 1,2-thiaza spiroring. If an idealized geometry of the naphthalene ring were taken into account, the S–N distance would be about 2.48 Å, which is very far from the almost covalent S–N bond length of 1.73 Å observed for the spiro-λ^4-sulfanes (**2**) and (**6**) with axial N and O heteroatoms. Nevertheless, the bond angle distortions of the peri-substituted naphthalene ring in compound (**3**) lead to a compromise: the axial nitrogen can approach the central sulfur by 1.80 Å. In the 1,2-thiaza spiroring the actual bond angles involving the naphthalene carbon atoms are 111°, 117° and 110°, instead of the idealized 120°. The rather long ''covalent'' S–N bond in the naphthalene derivative (**3**) is associated with a rather short ''polarized hypervalent'' S–O bond (2.07 Å), so that the *r*(N–S–O) distance of 3.87 Å in (**3**) corresponds to the similar values observed for other spiro-λ^4-sulfanes with axial nitrogen and oxygen heteroatoms. S–N and S–O bond lengths suggest that the zwitterionic character of compound (**3**) (see the limiting structure (**3A**)) is less pronounced than that of compound (**2**).

In spiro-λ^4-sulfanes (**1–3**) the equatorial S–C_{ar} bond lengths (1.79–1.81 Å) correspond to the usual values observed for S(IV)–C_{ar} bonds.

3.3. Conformation of spiro-λ^4-sulfane rings

The 1,2-thiazoline spirorings (rings A) in spiro-λ^4-sulfanes (**1–3**) are practically planar with maximum torsion angles $\varphi_{max} = 5°$, 7° and 2°, respectively (cf. $\varphi_{max} = 16°$ in (**5**) and 6° in (**6**)). The endocyclic amide parts in *N*-acetyl-substituted spiro-λ^4-sulfane (**1**) are of single-*trans* conformation: (ϕ(S–N–C=O) = –174°. The ''endocyclic'' C(7)=O(1) bond (1.21 Å) is shorter, whereas the C(7)–N(1) bond is longer (1.38 Å) than the corresponding bonds in the *N*-alkyl-substituted spiro-λ^4-sulfane (**5**) (1.23 and 1.34 Å). The difference may be explained by the fact that the lone pair of the nitrogen atom carrying two acyl groups in compound (**1**) is less involved in endocyclic amide conjugation than in the case of monoacyl derivative (**5**).

The 1,2-oxathiole spirorings (rings B) in spiro-λ^4-sulfanes (**2**) and (**3**) are not far from being planar with maximum torsion angles $\varphi_{max} = 12°$ and 1°, respectively (cf. $\varphi_{max} = 6°$ in (**4**) and 16° in (**6**)). In compounds (**2**) and (**6**) ring B assumes a flattened envelope form with O(2) in (**2**) and S(1) in (**6**) on the flap. Owing to the zwitterionic character of the unsymmetric spiro-λ^4-sulfanes (**2**) and (**3**) as well as that of the analogous compound (**6**) described earlier [2], the C=O double bonds in acyloxy moieties are longer (1.23, 1.22 and 1.21 Å, respectively), whereas the C–O single bonds are shorter (1.26, 1.29 and 1.29 Å, respectively) than the corresponding bonds in the symmetric spiro-λ^4-(diacyloxy)-sulfane (**4**) with two equivalent S–O hypervalent bonds (1.19 Å for C=O

Table 5
Relevant geometric parameters for compound (**3**) with ESDs in parentheses

Spirorings			
Interatomic distances (Å)	A		B
S(1)···O(3)	2.705(1)	S(1)–O(2)	2.066(1)
S(1)–N(1)	1.804(1)	S(1)–C(11)	1.808(1)
S(1)–C(1)	1.794(2)	C(11)–C(12)	1.389(2)
C(1)–C(9)	1.402(2)	C(12)–C(17)	1.488(2)
C(8)–C(9)	1.405(2)	C(17)–O(2)	1.294(2)
C(8)–N(1)	1.411(2)	C(17)–O(1)	1.219(2)
C(18)–N(1)	1.382(2)		
C(18)–C(19)	1.491(2)		
C(18)–O(3)	1.217(2)		
Bond angles			
Spirorings	A		B
N(1)-S(1)-O(2)	177.2(1)	O(2)-S(1)-C(11)	83.7(1)
N(1)-S(1)-C(1)	88.4(1)	S(1)-C(11)-C(12)	114.7(2)
S(1)-C(1)-C(9)	111.0(2)	C(11)-C(12)-C(17)	116.9(2)
C(1)-C(9)-C(8)	116.6(2)	C(12)-C(17)-O(2)	111.6(2)
C(9)-C(8)-N(1)	109.6(2)	C(17)-O(2)-S(1)	113.1(2)
C(8)-N(1)-S(1)	114.3(2)	O(2)-S(1)-C(1)	88.9(1)
N(1)-S(1)-C(11)	97.6(1)		
C(1)-S(1)-C(11)	103.4(1)		
Exocyclic parts	A		B
C(8)-N(1)-C(18)	132.5(2)	C(12)-C(17)-O(1)	123.2(3)
N(1)-C(18)-C(19)	119.8(2)	O(2)-C(17)-O(1)	125.3(3)
N(1)-C(18)-O(3)	117.7(2)		
O(3)-C(18)-C(19)	122.5(2)		
C(18)-N(1)-S(1)	112.1(2)		
S···O close contact	A		B
O(3)···S(1)-N(1)	54.9(1)	O(3)-S(1)-O(2)	127.8(1)
O(3)···S(1)-C(1)	143.1(1)	O(3)···S(1)-C(11)	86.1(1)
S(1)···O(3)-C(18)	74.5(2)		
Torsion angles (°)			
Spirorings	A		B
S(1)-C(1)-C(9)-C(8)	− 1.7(2)	S(1)-C(11)-C(12)-C(17)	− 0.5(2)
C(1)-C(9)-C(8)-N(1)	0.2(2)	C(11)-C(12)-C(17)-O(2)	0.8(2)
C(9)-C(8)-N(1)-S(1)	1.4(1)	C(12)-C(17)-O(2)-S(1)	− 0.6(1)
C(8)-N(1)-S(1)-C(1)	− 2.0(2)	C(17)-O(2)-S(1)-C(11)	0.3(2)
N(1)-S(1)-C(1)-C(9)	2.0(2)	O(2)-S(1)-C(11)-C(12)	0.1(2)
Aromatic ring positions	A		B
C(9)-C(1)-S(1)-C(11)	99.5(2)	C(12)-C(11)-S(1)-C(1)	87.5(2)
C(9)-C(1)-S(1)-O(2)	− 177.3(2)	C(12)-C(11)-S(1)-N(1)	177.7(2)
C(2)-C(1)-S(1)-C(11)	− 81.1(2)	C(16)-C(11)-S(1)-C(1)	− 94.4(2)
C(2)-C(1)-S(1)-O(2)	2.1(2)	C(16)-C(11)-S(1)-N(1)	− 4.2(2)
Acylamino part	A	Acyloxy part	B
C(9)-C(8)-N(1)-C(18)	167.9(3)	C(11)-C(12)-C(17)-O(1)	− 179.3(3)
C(8)-N(1)-C(18)-C(19)	2.8(2)	S(1)-O(2)-C(17)-O(1)	179.4(5)

Table 5 Continued

Spirorings	
C(8)-N(1)-C(18)-O(3)	− 178.6(3)
S(1)-N(1)-C(18)-C(19)	169.5(3)
S(1)-N(1)-C(18)-O(3)	− 11.9(2)
S···O close contact	A
N(1)-C(18)-O(3)···S(1)	7.6(1)
C(18)-O(3)···S(1)-N(1)	− 6.3(2)
O(3)···S(1)-N(1)-C(18)	5.7(1)

and 1.32 Å for C–O). In unsymmetric spiro-λ^4-sulfanes the tendency of C–O bond equalization resembles the carboxylate group.

3.4. Orientation of aromatic rings

The torsion angles $\varphi(C_{ar}-C_{ar}-S-C_{ar})=94°$, 95° and 100/88° obtained for compounds (**1**), (**2**) and (**3**), respectively, show that the aromatic rings fused with the heterocyclic spirorings are nearly perpendicular to the C_{ar}–S–C_{ar} plane, like other spiro-λ^4-sulfanes, e.g. (**4**), (**5**) and (**6**) with $\varphi(C_{ar}-C_{ar}-S-C_{ar})=96°$, 100/80° and 102°, respectively.

3.5. Intramolecular S···O close contacts

The axial nitrogen atoms in spiro-λ^4-sulfanes (**1–3**) bear an *N*-acetyl substituent. In all three cases the exocyclic amide parts assume a near single-*cis* conformation with the exocyclic torsion angles $\varphi(S-N-C{=}O)=-21°$, −7° and −12°, respectively. The almost eclipsed conformations allow the central sulfur and the exocyclic carbonyl-oxygen in (**1**), (**2**) and (**3**) to approach one another by 2.90, 2.73 and 2.71 Å, respectively, i.e. by a distance which is much shorter than the sum of the van der Waals radii 3.25 Å [7]. The relatively short S···O distances characterizing these particular cases of 1,4-type sulfur–oxygen nonbonded interaction may be ascribed to a short ''central'' S–N bond (cf. Formula 45 and Table 9 in Ref. [4]).

As can be seen in Fig. 1, Fig. 2 and Fig. 3, the trigonal bipyramidal geometry of the central sulfur in spiro-λ^4-sulfanes (**1–3**) is not affected appreciably by an irregular nonbonded coordination of the exocyclic carbonyl-oxygens to the sulfur atom. The carbonyl-oxygen approaching the central sulfur from the side of the sulfur lone pair lies nearer to the ring A′ or B than to ring A, as shown by the angles $\vartheta_{A'/B}$ $(C_{ar}-S\cdots O)=84°$, 72° and 75°, and $\vartheta_A(C_{ar}-S\cdots O)=136°$, 143° and 143°, observed in compounds (**1**), (**2**) and (**3**), respectively. The N-S···O angles (51°, 55° and 55°, respectively) are far from being rectangular, indicating that the exocyclic carbonyl-oxygen rises markedly above the C_{ar}–S–C_{ar} equatorial plane. In spiro-λ^4-sulfanes (**1–3**) the slight deviation of the exocyclic torsion angles φ_A(S-N-C=O) from the $\varphi=0$ value, which would point to an ideal eclipsed conformation, may be ascribed to a repulsion caused by the sulfur lone pair. Owing to the given position of the exocyclic carbonyl-oxygens, the O···S···O angle in the symmetric spiro-λ^4-sulfane (**1**) with two *N*-acetyl groups is not linear but assumes a value of 122°.

The C–N bond lengths (1.40, 1.38 and 1.38 Å) in the exocyclic amide part of spiro-λ^4-sulfanes (**1–3**) are significantly greater than the average value of 1.33 Å obtained for *N*-substituted amides [10], whereas the C=O bond lengths (1.22 Å for all) correspond to the expected value (1.23 Å in Ref. [21]). It seems very likely that the decrease of the conjugative effect in the exocyclic amide part is associated with the S···O close contact involving the carbonyl-oxygen of the amide group.

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