

# Spiro- $\lambda^4$ -sulfanes with O-ligands of different electronegativity in axial positions. A comparison of $\text{CH}_2\text{O}-\text{S}^{\text{IV}}-\text{OCO}$ and $\text{CH}_2\text{O}-\text{S}^{\text{IV}} \cdots \text{O}=\text{C}$ bond systems

2 PERKIN

Dénes Szabó,<sup>a</sup> István Kapovits,<sup>\*,a</sup> Gyula Argay,<sup>b</sup> Mátyás Czugler,<sup>b</sup>  
Alajos Kálmán<sup>\*,b</sup> and Tibor Koritsánszky<sup>b</sup>

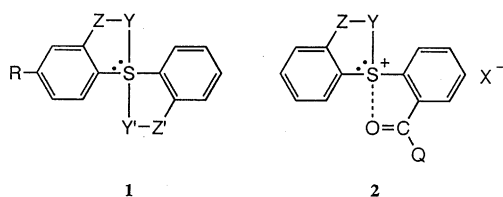
<sup>a</sup> Department of Organic Chemistry, L. Eötvös University, H-1518 Budapest 112,  
PO Box 32, Hungary

<sup>b</sup> Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest,  
PO Box 17, Hungary

Two novel diaryl(alkoxy)(acyloxy)spiro- $\lambda^4$ -sulfanes (**3** and **5**) exhibiting isomerism in relation to swapping of the five- and six-membered spiro-rings and two analogous cyclic alkoxy-sulfonium salts (**4** and **6**) with intramolecular  $\text{S} \cdots \text{O}$  interaction have been prepared and their molecular structures determined by X-ray diffraction. In all cases the arrangement of the ligands about the central sulfur atom shows a slightly distorted trigonal bipyramidal (TBP) geometry. In unsymmetrical spiro- $\lambda^4$ -sulfanes the  $\text{S}-\text{O}$ (alkoxy) and the considerably polarized  $\text{S}-\text{O}$ (acyloxy) bond lengths are 1.686(2) and 2.109(2) Å for **3** and 1.683(2) and 2.047(2) Å for **5**, respectively. In the analogous cyclic sulfonium salts the corresponding interatomic distances are 1.645(3) and 2.255(3) Å for **4** and 1.616(2) and 2.349(2) Å for **6**, respectively. The sums of the individual  $\text{S}-\text{O}$  interatomic distances found in the investigated spiro- $\lambda^4$ -sulfanes and cyclic alkoxy-sulfonium salts are 3.795(2) and 3.730(2) Å for **3** and **5**, whereas they are 3.900(3) and 3.965(2) Å for **4** and **6**, showing a significant difference between the two intervals. The individual  $\text{S}-\text{O}$ (alkoxy),  $\text{S}-\text{O}$ (acyloxy),  $\text{S} \cdots \text{O}$ (carbamoyl) and  $\text{S}-\text{C}_{\text{ar}}$  bond lengths, as well as the  $\text{C}_{\text{ar}}-\text{S}-\text{C}_{\text{ar}}$  bond angles are compared and discussed. The five- and six-membered spiro-rings assume a flattened envelope and a somewhat inverted half-chair conformation, respectively. The almost linear  $\text{O}-\text{S}-\text{O}$  bond system is not affected significantly by the different size of the spiro-rings except the case of sulfur-oxygen nonbonded interaction.

It has been well demonstrated that the hypervalent bond polarization in unsymmetrical  $\lambda^4$ -sulfanes (earlier 'sulfuranes'; e.g. **1**) is controlled by the different electronegativity of the axial ligands.<sup>1-4</sup> It has been also published, that cyclic sulfonium salts with  $\text{S} \cdots \text{O}$  interactions (e.g. **2**) show molecular structures of

alkoxy-sulfonium salts with  $\text{S} \cdots \text{O}$  interactions having the same axial array of oxygen atoms as in the above described sulfanes, we prepared two spiro- $\lambda^4$ -sulfanes (**3** and **5**) and their cyclic alkoxy-sulfonium salt analogues (**4**† and **6**) and determined the

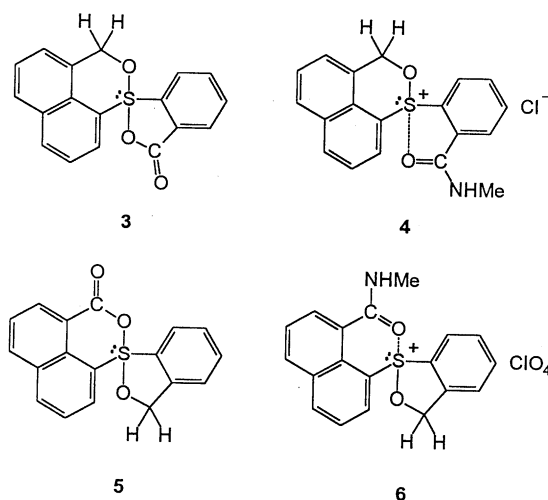


Z, Z' =  $\text{CH}_2$ ,  $\text{C}(\text{CH}_3)_2$ ,  $\text{C}(\text{CF}_3)_2$ ,  $\text{C}=\text{O}$ ; Y, Y' = O,  $\text{NCH}_3$

Q =  $\text{NHCH}_3$ ; R = H,  $\text{C}(\text{CH}_3)_3$ ; X = Cl,  $\text{ClO}_4$

slightly or considerably distorted trigonal bipyramidal geometry about the central sulfur atom similarly to those ones found in analogous spiro- $\lambda^4$ -sulfanes.<sup>4-6</sup> On the other hand, a quantum chemical study<sup>7</sup> has found that the covalent character of the  $\text{S} \cdots \text{O}$  close contact can be 10–15% of a usual  $\text{S}-\text{O}$  single bond, depending on the constitution of the individual compounds studied. These findings suggest that the strongest 'bonding' between the nonbonded sulfur and oxygen atom may be regarded as a 'premature' hypervalent bond similar to those ones existing in certain axially unsymmetrical dioxy- $\lambda^4$ -sulfane derivatives (e.g. **1**, Y = Y' = O, Z  $\neq$  Z').

In order to obtain additional information about the nature of bonding systems existing in unsymmetrical spiro- $\lambda^4$ -sulfanes having oxygen atoms at axial positions, as well as in cyclic



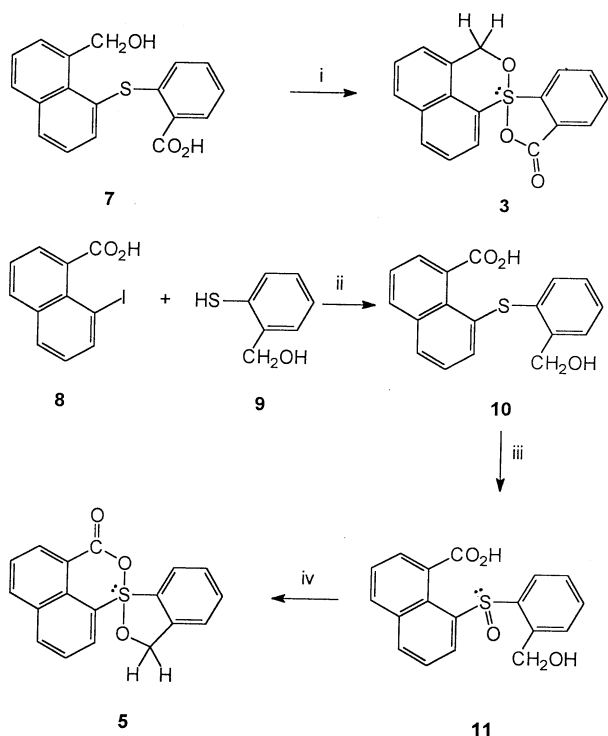
crystal structures. The results provided an opportunity to compare the structural parameters of the model compounds **3-6** and to study how the size of the spiro-rings influences the features of the molecular structures.

† A preliminary report on the crystal structure of **4** has been published in ref. 6.

## Results and discussion

### Syntheses

For the preparation of spiro- $\lambda^4$ -sulfane **3** (Scheme 1) 2-[8-(hydroxymethyl)-1-naphthylthio]benzoic acid<sup>8</sup> (**7**) was oxidized with dichloramine-T in pyridine under anhydrous conditions



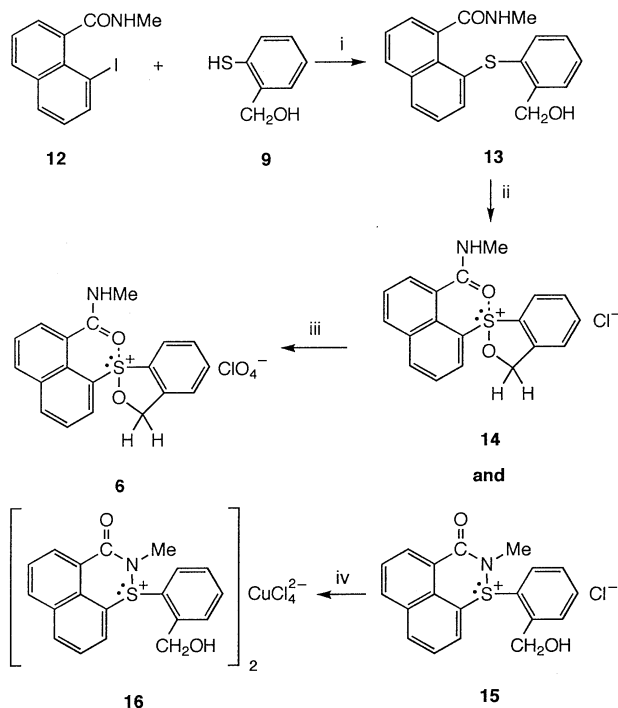
**Scheme 1** Reagents and conditions (i)  $\text{TsNCl}_2$ , pyridine, 20 °C, 12 h; (ii)  $\text{Cu}_2\text{O}$ , pyridine, reflux, 2 h, then HCl aq; (iii)  $\text{TsNClNa}\cdot 3\text{H}_2\text{O}$ ,  $\text{KHCO}_3$  (aq), 100 °C, 1 h, then HCl aq; (iv) DCC, dioxane, 20 °C, 1 h

(path i; *cf.* ref. 9). To obtain the spiro- $\lambda^4$ -sulfane **5** (Scheme 1) 8-iodo-1-naphthoic acid<sup>10</sup> (**8**) was first coupled with 2-mercaptobenzyl alcohol<sup>11</sup> (**9**) to give 8-[2-(hydroxymethyl)-1-phenylthio]-1-naphthoic acid (**10**; path ii; *cf.* ref. 8). Then the potassium salt of the sulfide carboxylic acid (**10**) was oxidized with chloramine-T in aqueous solution to give 8-[2-(hydroxymethyl)-1-phenylsulfinyl]-1-naphthoic acid (**11**; path iii; *cf.* ref. 12) which was finally submitted to an intramolecular dehydration (path iv) to give the spiro- $\lambda^4$ -sulfane **5**.

The cyclic alkoxy-sulfonium salt **4** was prepared by the procedure given in ref. 6. In the synthesis of the cyclic sulfonium salt **6** (Scheme 2), *N*-methyl-8-iodo-1-naphthamide<sup>8</sup> (**12**) was first coupled with 2-mercaptobenzyl alcohol<sup>11</sup> (**9**) to give *N*-methyl-8-[2-(hydroxymethyl)-1-phenylthio]-1-naphthamide (**13**; path i). The treatment of the sulfide **13** with  $\text{Bu}^t\text{OCl}$  (path ii, *cf.* ref. 6) resulted in a mixture of 1-[8'-(*N*-methylcarbamoyl)-1'-naphthyl]-3*H*-2,1-benzoxathiol-1-ium chloride (**14**; minor product) and 1-[2'-(hydroxymethyl)phenyl]-2-methyl-3-oxo-3*H*-1,2-naphtho[1,8-*d,e*]thiazin-1-ium chloride (**15**; major product). To get some of the crystals of **6**, an aliquot portion of the mixture of **14** and **15** was treated with  $\text{AgClO}_4$  (path iii) and then a few X-ray-quality crystals of **6** crystallized from the mixture. The sulfonium salt **15** could be separated by addition of  $\text{CuCl}_2$  to the mixture of **14** and **15** (path iv) leading to the formation of the complex cuprous salt **16**.

### Crystallographic analyses

The molecular structures for the spiro- $\lambda^4$ -sulfanes **3** and **5** as well as for the cyclic alkoxy-sulfonium salt analogues **4** and **6** were determined by single crystal X-ray diffraction methods. The stereoscopic views are shown in Figs. 1–4. Selected bond lengths, bond angles and torsion angles characteristic of compounds **3–6** are listed in Tables 1–3.



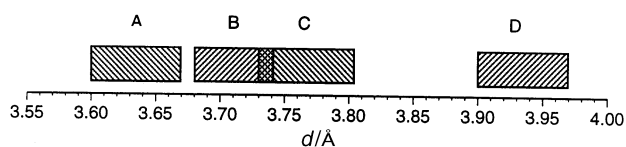
**Scheme 2** Reagents and conditions (i)  $\text{Cu}_2\text{O}$ , pyridine, reflux, 2 h, then HCl aq; (ii)  $\text{Bu}^t\text{OCl}$ ,  $\text{CH}_2\text{Cl}_2$ , 20 °C, 2 h; (iii)  $\text{AgClO}_4$ , MeOH, 20 °C, 2 h; (iv)  $\text{CuCl}_2$ , MeOH, 20 °C, 10 min

### Sulfur configuration

As shown by the stereoscopic views of the molecules **3–6** the structures can be described in terms of a slightly distorted trigonal bipyramidal arrangement of the ligands about the central sulfur (disregarding the anions for **4** and **6**), where the electro-negative oxygens are in the axial positions. In each  $\text{S}^{\text{IV}}\text{[O,O,C,C]}$  moiety the shorter S–O bond is tilted towards the sulfur lone pair, whereas the longer S–O bond is either bent towards the equatorial C(1)–S–C(12) angle (**3** and **6**), or tilted predominantly towards C(12) in the plane perpendicular to the sulfur lone pair (**5**), or remains axial (**4**). Consequently, apart from **3**, the axial O(1)–S–O(2) angles in comparison with the equatorial C(1)–S–C(12) angles are greater than 180°. The molecules of all four models **3–6** are chiral.

### Bond lengths and angles about the central sulfur

In a previous paper<sup>13</sup> we pointed out that in the series of symmetric diaryl(dialkoxy)spiro- $\lambda^4$ -sulfanes the O–S–O moiety with hypervalent bonds may be regarded as a structural unity and the sum of the individual S–O bond lengths (3.684–3.744 Å) characteristic of this type of spiro- $\lambda^4$ -sulfanes differs markedly (see A and B in Scheme 3) from the values found earlier for



**Scheme 3** Interatomic distances (Å) in axial O–S–O arrays of spiro- $\lambda^4$ -sulfanes. (A): (dialkoxy)spiro- $\lambda^4$ -sulfanes; (B): (diacyloxy)spiro- $\lambda^4$ -sulfanes; (C): (acyloxy)(alkoxy)spiro- $\lambda^4$ -sulfanes; (D): cyclic alkoxy-sulfonium salts with  $\text{S}\cdots\text{O}(\text{carbamoyl})$  close contact.

the symmetrical and unsymmetrical dialkoxy analogues<sup>3</sup> [**1**:  $\text{R} = \text{C}(\text{CH}_3)_3$ ,  $\text{Z} = \text{Z}' = \text{C}(\text{CF}_3)_2$ ,  $\text{Y} = \text{Y}' = \text{O}$ , 3.650 Å;  $\text{R} = \text{H}$ ,  $\text{Z} = \text{Z}' = \text{C}(\text{CH}_3)_2$ ,  $\text{Y} = \text{Y}' = \text{O}$ , 3.601 Å;  $\text{R} = \text{H}$ ,  $\text{Z} = \text{C}(\text{CH}_3)_2$ ,  $\text{Z}' = \text{C}(\text{CF}_3)_2$ ,  $\text{Y} = \text{Y}' = \text{O}$ , 3.668 Å] as well as for an unsymmetrical acyloxyalkoxy species<sup>3</sup> (**17**, 3.910 Å). Furthermore, a rather long interatomic distance (3.895 Å) was found in the

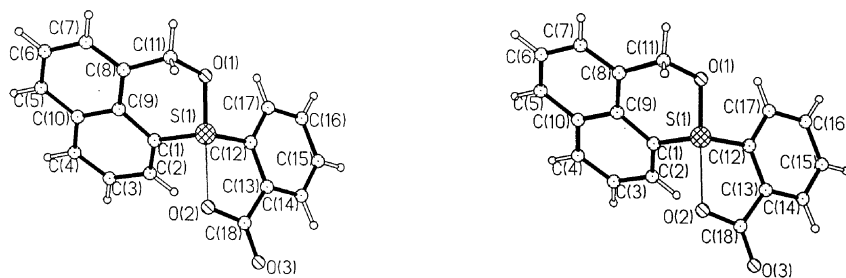


Fig. 1 Stereoscopic view of spiro- $\lambda^4$ -sulfane **3** with numbering scheme for nonhydrogen atoms

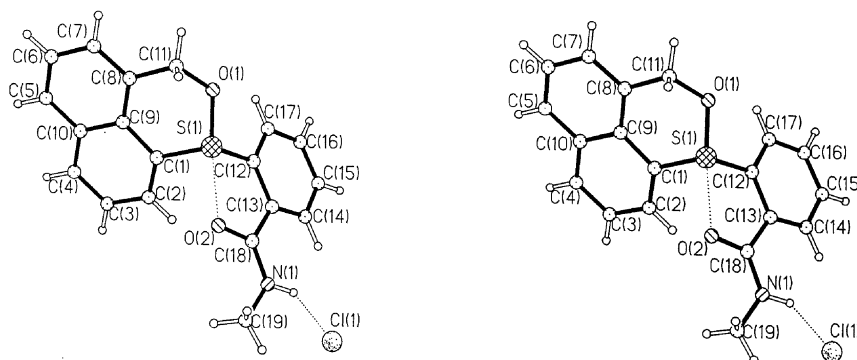


Fig. 2 Stereoscopic view of sulfonium salt **4** with numbering scheme for nonhydrogen atoms

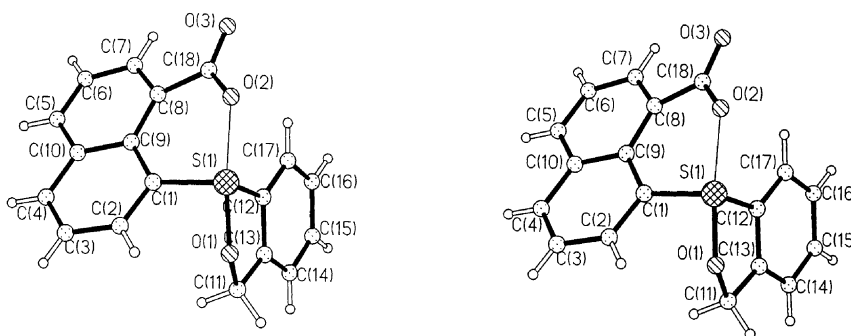


Fig. 3 Stereoscopic view of spiro- $\lambda^4$ -sulfane **5** with numbering scheme for nonhydrogen atoms

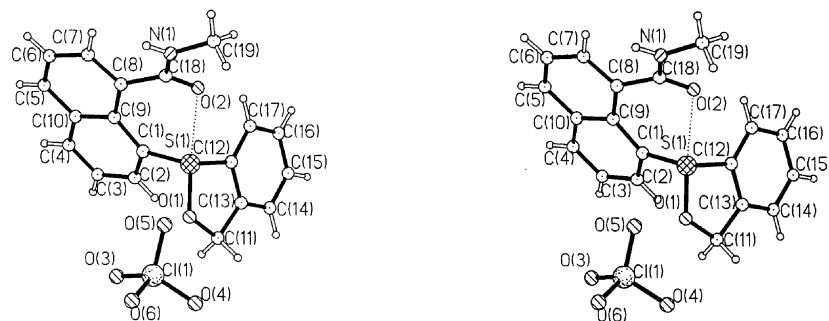
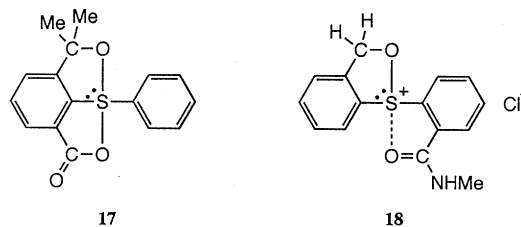


Fig. 4 Stereoscopic view of sulfonium salt **6** with numbering scheme for nonhydrogen atoms. The  $\text{ClO}_4^-$  anion is also shown

linear O(alkoxy)-S $\cdots$ O(carbamoyl) moiety of **18**† which is a cyclic alkoxy-sulfonium salt with S $\cdots$ O interaction. In view of these observations, a comparative structure analysis of two isomeric spiro- $\lambda^4$ -sulfanes (**3** and **5**) and their cyclic alkoxy-sulfonium salt analogues (**4** and **6**) with intramolecular S $\cdots$ O interactions enabled us to draw more detailed conclusions on how electronic and steric effects influence the nature of the bonds about the tetracoordinate S<sup>IV</sup> atom.

The interatomic O(alkoxy)-S-O(acyloxy) distances [1.686(2) + 2.109(2) = 3.795 Å for **3** and 1.683(2) + 2.047(2) =



3.730(2) for **5**) are in the region which is tightly joined to the upper end of the corresponding region of O(acyloxy)-S-O(acyloxy) systems (see B and C in Scheme 3). Although the indi-

† A preliminary report on the crystal structure of **18** has been published in ref. 5. The results in detail will be published elsewhere.

**Table 1** Relevant geometric parameters pertaining to the central sulfur atom with e.s.d. values in parentheses

	<b>3</b>	<b>4<sup>a</sup></b>	<b>5</b>	<b>6</b>
Interatomic distances/Å				
S(1)–O(1)	1.686(2)	1.645(3)	1.683(2)	1.616(2)
S(1)–O(2)	2.109(2)	2.255(3)	2.047(2)	2.349(2)
S(1)–C(1)	1.795(3)	1.796(4)	1.823(2)	1.803(3)
S(1)–C(12)	1.789(3)	1.799(3)	1.807(2)	1.787(3)
O(1)–C(11)	1.445(4)	1.455(5)	1.431(3)	1.459(4)
O(2)–C(18)	1.287(3)	1.244(5)	1.288(3)	1.246(4)
O(3)–C(18)	1.229(4)	—	1.227(3)	—
N(1)–C(18)	—	1.299(6)	—	1.316(5)
Bond angles (°)				
O(1)–S(1)–O(2)	178.4(1)	186.2(1)	186.3(3)	189.1(2)
C(1)–S(1)–C(12)	106.4(1)	104.8(2)	102.9(2)	102.6(3)
O(1)–S(1)–C(12)	94.8(1)	96.1(2)	—	—
O(2)–S(1)–C(12)	—	—	90.1(2)	88.4(2)
O(2)–S(1)–C(1)	88.0(1)	89.9(2)	—	—
O(1)–S(1)–C(1)	—	—	96.6(2)	102.2(2)
Torsion angles (°)				
S(1)–O(2)–C(18)–O(3)	169.6(3)	—	–155.9(6)	—
S(1)–O(2)–C(18)–N(1)	—	174.3(3)	—	121.9(1)
O(2)–S(1)–C(1)–C(9)	136.5(2)	145.0(3)	—	—
O(2)–S(1)–C(12)–C(13)	—	—	–173.3(4)	173.9(5)
O(1)–S(1)–C(12)–C(13)	170.7(2)	167.3(3)	—	—
O(1)–S(1)–C(1)–C(9)	—	—	–156.4(4)	136.4(5)
C(12)–S(1)–C(1)–C(9)	–140.5(2)	–134.4(3)	–65.4(3)	–127.4(3)
C(1)–S(1)–C(12)–C(13)	–94.5(2)	–94.8(3)	–83.7(3)	–100.4(5)

<sup>a</sup> A preliminary report on the crystal structure of **4** is published in ref. 6.

**Table 2** Endocyclic bond angles (°) pertaining to the spiro-rings with e.s.d. values in parentheses

	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Five-membered ring				
O(2)–S(1)–C(12)	83.8(1)	80.9(2)	—	—
O(1)–S(1)–C(12)	—	—	89.5(2)	93.3(2)
S(1)–O(2)–C(18)	110.8(2)	108.7(3)	—	—
S(1)–O(1)–C(11)	—	—	115.0(3)	116.4(4)
O(2)–C(18)–C(13)	112.1(2)	115.7(4)	—	—
O(1)–C(11)–C(13)	—	—	106.3(4)	106.2(5)
C(12)–C(13)–C(18)	117.1(2)	116.4(3)	—	—
C(12)–C(13)–C(11)	—	—	113.3(4)	114.8(5)
S(1)–C(12)–C(13)	114.5(2)	117.3(3)	110.3(3)	109.3(4)
Six-membered ring				
O(1)–S(1)–C(1)	93.3(1)	96.1(2)	—	—
O(2)–S(1)–C(1)	—	—	89.6(2)	86.1(2)
S(1)–O(1)–C(11)	106.7(2)	109.2(2)	—	—
S(1)–O(2)–C(18)	—	—	129.5(3)	104.9(4)
O(1)–C(11)–C(8)	110.4(2)	109.5(3)	—	—
O(2)–C(18)–C(8)	—	—	116.9(3)	119.1(5)
C(11)–C(8)–C(9)	119.8(3)	120.4(4)	—	—
C(18)–C(8)–C(9)	—	—	122.1(4)	121.0(5)
C(8)–C(9)–C(1)	123.2(3)	123.7(4)	126.9(4)	127.0(5)
S(1)–C(1)–C(9)	115.4(2)	116.6(3)	124.4(3)	120.7(4)

vidual S–O(alkoxy) distances (1.68–1.69 Å) are slightly shorter than the sum of the covalent radii (1.70 Å; ref. 14) the S–O(alkoxy) linkage in **3** and **5** may be regarded as a somewhat elongated covalent bond [*cf.* the S<sup>IV</sup>–O bond distance of 1.62 Å in ref. 15]. On the other hand, the unusually long S–O(acyloxy) distances (2.05–2.11 Å) can be attributed to a strong polarization of the usual S–O hypervalent bond (1.84–1.87 Å in ref. 13; *cf.* ref. 16).

The swapping of the five- and six-membered rings does not change considerably the axial O–S–O array of the isomeric spiro-λ<sup>4</sup>-sulfanes **3** ('6 + 5' spiro-rings) and **5** ('5 + 6' spiro-rings): Δ*r*(O–S–O) is not more than 0.065 Å.

A more detailed comparison of the ring-size effects would require the study of the analogous spiro-λ<sup>4</sup>-sulfane **1a** (R = H, Z = CH<sub>2</sub>, Z' = CO, Y = Y' = O) containing two five-membered

**Table 3** Endocyclic torsion angles (°) pertaining to the spiro-rings with e.s.d. values in parentheses

	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Five-membered ring				
O(2)–S(1)–C(12)–C(13)	–8.4(2)	–7.3(3)	—	—
O(1)–S(1)–C(12)–C(13)	—	—	12.9(3)	2.8(4)
S(1)–C(12)–C(13)–C(18)	4.4(3)	5.4(3)	—	—
S(1)–C(12)–C(13)–C(11)	—	—	–1.1(2)	–2.0(4)
C(12)–C(13)–C(18)–O(2)	6.2(4)	3.4(5)	—	—
C(12)–C(13)–C(11)–O(1)	—	—	–14.1(3)	0.1(5)
C(13)–C(18)–O(2)–S(1)	–12.0(3)	–8.3(4)	—	—
C(13)–C(11)–O(1)–S(2)	—	—	25.0(2)	2.1(3)
C(18)–O(2)–S(1)–C(12)	12.2(2)	9.1(3)	—	—
C(11)–O(1)–S(1)–C(12)	—	—	–22.5(3)	–2.9(4)
Six-membered ring				
O(1)–S(1)–C(1)–C(9)	–44.5(2)	–36.5(3)	—	—
O(2)–S(1)–C(1)–C(9)	—	—	24.6(3)	–39.9(4)
S(1)–C(1)–C(9)–C(8)	9.3(4)	4.8(5)	–7.8(3)	12.5(5)
C(1)–C(9)–C(8)–C(11)	5.5(4)	1.9(6)	—	—
C(1)–C(9)–C(8)–C(18)	—	—	–13.9(4)	14.1(5)
C(9)–C(8)–C(11)–O(1)	25.6(4)	30.6(5)	—	—
C(9)–C(8)–C(18)–O(2)	—	—	3.5(4)	22.2(6)
C(8)–C(11)–O(1)–S(1)	–71.4(3)	–71.4(4)	—	—
C(8)–C(18)–O(2)–S(1)	—	—	26.6(2)	–60.2(8)
C(11)–O(1)–S(1)–C(1)	75.7(2)	69.6(3)	—	—
C(18)–O(2)–S(1)–C(1)	—	—	–37.5(3)	66.2(4)

spiro-rings. Unfortunately, we could not grow X-ray-quality crystals from racemic **1a**. However, the molecular structure of one of its enantiomers ( $[\alpha]_{546.1}^{25} +31.2$ , *c* 0.5 in dimethylformamide) could be determined with S–O(alkoxy) 1.706(3), S–O(acyloxy) 2.051(3) [sum 3.757(3)] and C=O 1.230 Å interatomic distances and with the axial O–S–O bond angle of 179.7(2)°. As can be seen, data found for the O(alkoxy)–S–O(acyloxy) moiety in optically active **1a**§ ('5 + 5' spiro-rings) do not differ markedly from those obtained for **3** and **5**.

§ The results obtained for **1a** will be published in detail elsewhere together with the molecular structures of other optically active spiro-λ<sup>4</sup>-sulfanes.

In the case of cyclic alkoxyulfonium salts exhibiting S...O close contact the following interatomic distances were found for the linear O(alkoxy)-S...O(carbamoyl) moiety: 1.645(3) + 2.255(3) = 3.900 Å in **4** ('6 + 5' spiro-rings), 1.616 + 2.349(2) = 3.965 Å in **6** ('5 + 6' spiro-rings) and 1.635(2) + 2.260(2) = 3.895 Å in **18** ('5 + 5' spiro-rings; see ref. 5). All these data reveal that spiro- $\lambda^4$ -sulfanes and analogous cyclic acyloxysulfonium compounds with S...O close contact can be well distinguished by the geometry of the O(1)-S-O(2) arrays (see C and D in Scheme 3). Because the overall conformations of these two types of compounds are very similar (see e.g. Figs. 1 and 2 for **3** and **4**) the difference  $\Delta r = 0.1-0.2$  Å in  $r[\text{O}(1)-\text{S}-\text{O}(2)]$  values can be attributed to different electronic structures.

The sulfonium structure is convincingly shown by the short S-O(alkoxy) distances found for **4**, **6** and **18** (1.62-1.65 Å). The cationic character of the central sulfur atom is not shielded markedly by the slight electron-releasing effect of the carbonyl-O(2) atoms (see ref. 7) which are rather distant in the axial direction. The long S(1)-O(2) intramolecular distances (2.26-2.35 Å) may be attributed to an effective S...O close contact (the sum of the van der Waals radii is 3.25 Å, see refs. 7 and 16) rather than an elongated (polarized) weak hypervalent bond.

In contrast with spiro- $\lambda^4$ -sulfanes the bonding system in the spiro-rings of the analogous cyclic alkoxyulfonium compounds depends on the ring size. While S-O(alkoxy) bond lengths are nearly the same, the S...O(carbamoyl) close contacts are longer in six-membered rings than in the five-membered analogues ( $\Delta r = 0.1-0.3$  Å). This result is consistent with earlier findings suggesting that a six-membered ring is not favourable for an effective S...O close contact (see ref. 16). In the case of compound **6** the significant elongation of the S...O nonbonded distance may also be related with an unfavourable orientation of the planar carbamoyl moiety in respect to the positively charged sulfur atom; the S(1)-O(2)-C(18)-N(1) torsion angle is 122° for **6** (six-membered ring in Fig. 4), whereas it is 174° for **4** (five-membered ring in Fig. 2).

The C=O distances [1.229(4), 1.227(3) and 1.230(11) Å] found for **3**, **5** and **1a**, respectively, show significant elongations relative to the average C=O bond lengths obtained for the corresponding  $\gamma$ - and  $\delta$ -lactones (1.201 and 1.205 Å in ref. 17) and resemble those found in  $\text{ArCO}_2^-$  compounds (1.255 Å in ref. 17). Accordingly, the carbonyl stretching frequencies are rather low: 1653 and 1625  $\text{cm}^{-1}$  for **3** and **5**, respectively. All these data point to a conjugative interaction between the carbonyl group and the negatively polarized O(acyloxy) atom, which gives some zwitterionic character for unsymmetrical spiro- $\lambda^4$ -sulfanes **3**, **5** and **1a** (see refs. 2-4).

Owing to the intramolecular  $\text{S}^+ \cdots \text{O}(\text{carbamoyl})$  interaction in the cyclic alkoxyulfonium compounds **4**, **6** and **18** (in which the carbonyl-oxygen is an electron-donor) the *o*-carbamoyl group is polarized resulting in a significant elongation of the C=O bond [1.244(5), 1.246(4) and 1.258(2) Å, respectively] and in a shortening of the C-N bond [1.299(6), 1.316(5) and 1.308(3) Å, respectively]; cf. the average bond lengths obtained for C=O (1.234 Å) and C-N(R) bonds (1.334 Å) in *N*-substituted amides.<sup>17</sup> As expected, the amide stretching frequencies are significantly lower than normal values: 1625 and 1622  $\text{cm}^{-1}$  for **4** and **6**, respectively.

The equatorial S(1)-C(1) and S(1)-C(12) bond lengths in **3-6**, ranging from 1.783(2) to 1.823(2) Å (average 1.800 Å), are similar to the average values obtained for symmetrical diaryl(diacyloxy)-spiro- $\lambda^4$ -sulfanes (1.785 Å),<sup>13</sup> symmetrical and unsymmetrical diaryl(dialkoxy)-spiro- $\lambda^4$ -sulfanes (1.803 Å),<sup>3</sup> as well as for the unsymmetrical  $\text{S}^{\text{IV}}[\text{O}, \text{N}, \text{C}, \text{C}]$  type of spiro- $\lambda^4$ -sulfanes and their cyclic sulfonium salt analogues (1.799 Å).<sup>4</sup> The  $\text{C}_{\text{ar}}-\text{S}-\text{C}_{\text{ar}}$  bond angle in the spiro- $\lambda^4$ -sulfanes **3**, **5** and **1a** (105-106°) is somewhat larger than those in the cyclic acyloxysulfonium salts **4**, **6** and **18** (102-103°).

**Table 4** Puckering parameters<sup>18</sup> for the six-membered spiro-rings with e.s.d. values in parentheses

Compound	$Q/\text{Å}$	$\vartheta(^{\circ})$	$\phi(^{\circ})$	Canonical forms
<b>6</b>	0.750(4)	123.2(3)	208.5(5)	${}^2\text{H}_1$ ( ${}^2\text{S}_1$ )
<b>3</b>	0.707(4)	126.5(3)	217.8(4)	${}^2\text{H}_1$
<b>4</b>	0.640(10)	127.6(9)	227.4(10)	${}^2\text{E}$
<b>5</b>	0.386(3)	64.5(4)	14.2(5)	${}^1\text{S}_2$ ( ${}^1\text{E}$ )

### Conformations of spiro-rings

As shown by torsion angles in Table 3 the conformation of the five-membered spiro-rings vary from planar in **6** ( $\phi_{\text{max}} = -3^{\circ}$ ) to a twisted envelope shape in **5** ( $\phi_{\text{min}} = -1^{\circ}$ ;  $\phi_{\text{max}} = 12^{\circ}$ ) with S(1) on the flap. Compounds **3** ( $\phi_{\text{min}} = 4^{\circ}$ ;  $\phi_{\text{max}} = 25^{\circ}$ ) and **4** ( $\phi_{\text{min}} = 3^{\circ}$ ;  $\phi_{\text{max}} = 9^{\circ}$ ) assume a flattened envelope form with O(2) on the flap. Similar conclusions can be drawn from the puckering amplitudes<sup>18</sup>  $Q = 0.032(4)$  Å for **6**, 0.111(9) for **4**, 0.140(3) Å for **3** and 0.238(3) for **5**, as well.

Torsion angles in Table 3 indicate that the six-membered spiro-rings in compounds **3-6** assume a more or less inverted half-chair form. The six-membered ring conformations in **3** ( $\phi_{\text{min}} = 5^{\circ}$  and  $9^{\circ}$ ;  $\phi_{\text{max}} = -71^{\circ}$  and  $76^{\circ}$ ), **4** ( $\phi_{\text{min}} = 2^{\circ}$  and  $5^{\circ}$ ;  $\phi_{\text{max}} = -71^{\circ}$  and  $70^{\circ}$ ) and **6** ( $\phi_{\text{min}} = 13^{\circ}$  and  $14^{\circ}$ ;  $\phi_{\text{max}} = -60^{\circ}$  and  $66^{\circ}$ ) may be classified as a 1,2-diplanar forms and that in **5** ( $\phi_{\text{min}} = -8^{\circ}$ ,  $-14^{\circ}$  and  $4^{\circ}$ ;  $\phi_{\text{max}} = -38^{\circ}$ ) as a 1,3 diplanar form (see Scheme 7 and Fig. 17 in ref. 19).

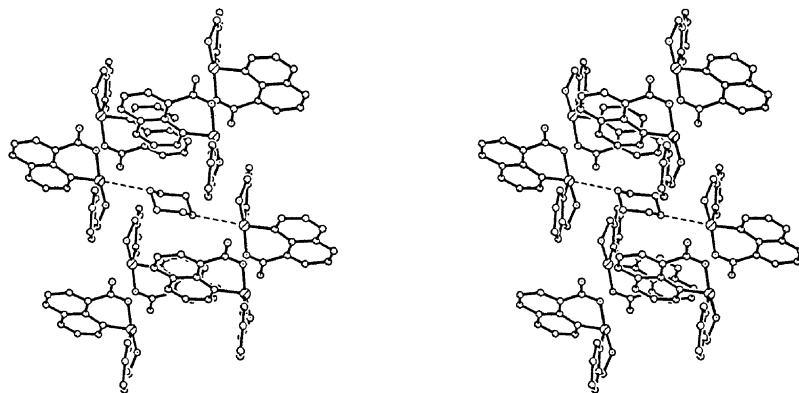
If we start from the puckering parameters listed in Table 4, the six-membered spiro-ring of **3** may be classified as  ${}^2\text{H}_1$  half-chair which is slightly distorted towards either an envelope in **4** or a skew-boat in **6**. In contrast, **5** assumes a rather flat transitional structure between the canonical forms  ${}^1\text{S}_2$  and  ${}^1\text{E}$ , related inversely to the others.

The overall conformation of the butterfly-like molecules **3-6** with the  $\text{C}_{\text{ar}}-\text{S}-\text{C}_{\text{ar}}$  moiety is characterized by the dihedral angle formed by the planar aryl groups. This angle varies in a narrow range, 73-77°, for **3**, **4** and **6**, whereas it approaches to 90° in **5**. However, as shown by the torsion angle C(2)-C(1)-S(1)-C(12) = 113.3(2)° for **5** vs. 42.0(3), 46.9(4) and 59.1(4)° found in **3**, **4** and **6**, respectively, the degree of rotation of the naphthyl ring around the S(1)-C(1) bond in **5** differs from those found in the other three molecules. The phenyl rings with a mean dihedral angle of 84.3(3)° are nearly perpendicular to the central C(1)-S(1)-C(12) planes. The acyloxy (O-C=O) group in **3** and the carbamoyl (O=C-NHMe) group in **4** lie approximately in the plane of the phenyl ring, whereas the interplanar angle with the naphthyl ring is 13° in **5** and 29° in **6**. The unfavourable twisting of the carbamoyl group, which makes the S...O interaction weaker (*vide supra*), is also reflected by the interplanar angle with the central C(1)-S(1)-C(12) plane [38.6(2)° for **6** and 87.0° for **4**].

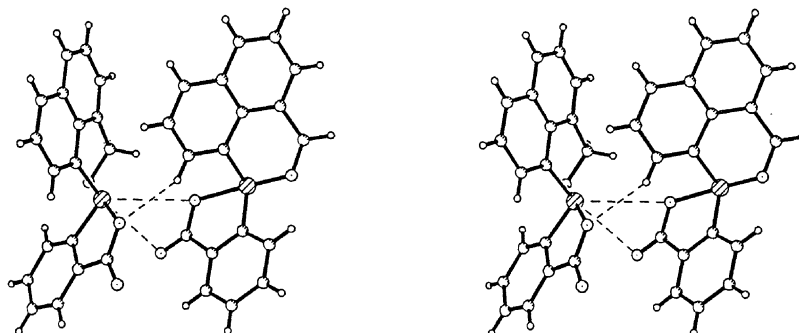
### Crystal structures

Two of the bulky and butterfly-like molecules form inclusion compounds with solvent molecules (dichloromethane for **4** and dioxane for **5**). In **5** a dioxane molecule sitting around a centre of symmetry  $1(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  acts as a guest partner with oxygen atoms directed to the same centre of symmetry related to sulfur atoms (Fig. 5). The two intermolecular S...O contacts formed [3.105(2) Å] are somewhat shorter than the sum of the van der Waals radii (3.25 Å) and they are almost collinear with S-aryl bonds,  $\text{O} \cdots \text{S}-\text{C} = 174.9(2)^{\circ}$ .

The molecule in the general position is also the recipient of a second (longer) intermolecular S...O contact [with an S...O distance of 3.355(1) Å and with an  $\text{O} \cdots \text{S}-\text{C}$  angle of 174.5(1)°] from an axial O atom of the molecule related by another centre of symmetry at  $(0, 0, \frac{1}{2})$ . These two non-bonded interactions, approximately perpendicular to each other [ $\text{O} \cdots \text{S} \cdots \text{O} = 104.7(1)^{\circ}$ ], close a distorted octahedron about the sulfur atom. As shown in Fig. 6 there is also a 'short



**Fig. 5** Stereoscopic view of the packing of the coordinatoclathrate **5** with its guest molecule: dioxane. Only the stronger  $S \cdots O$  contacts are shown by dashed lines



**Fig. 6** Stereoscopic view of the packing of **3** showing both intermolecular  $S \cdots O$  contacts and the hydrogen bond of  $CH \cdots O$  type

intermolecular  $S \cdots O$  contact' [with an  $S \cdots O = 3.072(1)$  Å distance and with an  $O \cdots S-C = 166.9(2)^\circ$  angle] between the glide-plane-related molecules of **3**. It is donated by the carbonyl oxygen and accompanied by a 'long  $S \cdots O$  contact' of  $3.431(1)$  Å from the adjacent bridging axial O. However, the  $O \cdots S \cdots O$  angle between these contacts is only  $39.9(1)^\circ$ . Simultaneously, the axial oxygen is the acceptor in a hydrogen bond of  $CH \cdots O$  type [ $C \cdots O = 3.332(2)$ ,  $H \cdots O = 2.505(4)$  Å,  $CH \cdots O = 148.1(5)^\circ$ ]. The net effect of these intermolecular interactions on the  $O-S-O$  moieties is the subject of further studies (*e.g.* cocrystallization of **3** with dioxane, resolution of **5**, *etc.*) In the cyclic sulfonium salt **4** dichloromethane molecules occupy the voids formed among the bulky sulfonium cations and their chloride anions. The  $Cl^-$  anion is separated from  $S^+$  by  $4.272(1)$  Å and participates in an  $NH \cdots Cl$  hydrogen bond [ $N \cdots Cl = 3.106(4)$ ,  $H \cdots Cl = 2.31(1)$  Å,  $NH \cdots Cl = 154.1(7)^\circ$ ] as an acceptor. In **6** the tetrahedral  $ClO_4^-$  anions exhibit positional disorder; the shortest  $(Cl)O \cdots S^+$  distance is  $3.72(1)$  Å and the  $Cl(O)S \cdots C(12)$  angle is  $157.6(3)^\circ$ .

### Conclusions

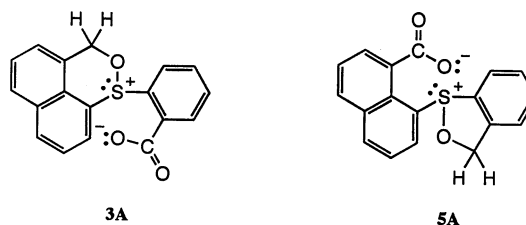
It was possible to prepare unsymmetrical diaryl(acyloxy)-(alkoxy)spiro- $\lambda^4$ -sulfanes (**3** and **5**) of  $S^{IV}[C,C,O,O]$  type and analogous cyclic alkoxy-sulfonium salts with  $S \cdots O$  interaction (**4** and **6**), in which the axial arrays of the oxygen and sulfur atoms are the same; **3** and **5**, as well as **4** and **6**, exhibit isomerism in relation to swapping of the five- and six-membered spiro-rings. By X-ray structure determinations we compared the geometric parameters about the central tetravalent sulfur establishing the resemblances and differences in molecular structures.

It may be concluded that (i) in all of the cases investigated the arrangements of the ligands about the central sulfur can be described in terms of a slightly distorted trigonal bipyramidal geometry with electronegative oxygen atoms in axial positions.

(ii) Spirosulfuranes with an unsymmetrical axial  $O(\text{alkoxy})-S-O(\text{acyloxy})$  array can be well distinguished both from the symmetrical  $O(\text{alkoxy})-S-O(\text{alkoxy})$  and  $O(\text{acyloxy})-S-O(\text{acyloxy})$  analogues and from cyclic alkoxy-sulfonium compounds with  $S \cdots O$  close contact; distinction can be made by the different regions of  $r(O-S-O)$  distances:  $3.73-3.80$ ,  $3.60-3.67$ ,  $3.68-3.74$  and  $3.90-3.97$  Å, respectively.

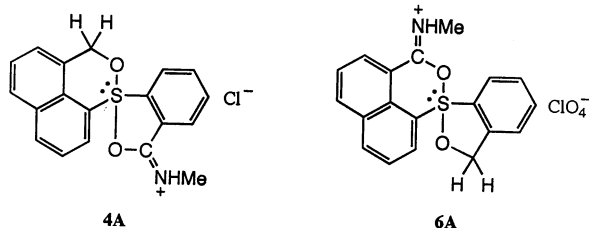
(iii) The  $S-O(\text{alkoxy})$  bond in unsymmetrical spiro- $\lambda^4$ -sulfanes ( $1.68-1.71$  Å) is shorter than in symmetrical analogues ( $1.81-1.82$  Å), but longer than in cyclic alkoxy-sulfonium compounds ( $1.62-1.65$  Å) pointing to a somewhat elongated (weakened)  $S-O(\text{alkoxy})$  covalent bond.

(iv) The  $S-O(\text{acyloxy})$  bond in unsymmetrical spiro- $\lambda^4$ -sulfanes ( $2.05-2.11$  Å) is markedly longer than in symmetrical diacyloxy analogues ( $1.84-1.87$  Å) indicating the strong polarization of the  $S-O(\text{acyloxy})$  hypervalent bond which is enhanced by a conjugative interaction with the carbonyl part of the acyloxy group. All these effects give pronounced 'alkoxy-sulfonium-carboxylate zwitterion character' to unsymmetrical spiro- $\lambda^4$ -sulfanes, which may be described *e.g.* by the major contribution of the limiting structures **3A** and **5A**.



(v) The  $S \cdots O$  nonbonded distance ( $2.26-2.35$  Å) in cyclic alkoxy-sulfonium compounds stabilized by  $S \cdots O$  close contact is surprisingly short revealing a strong interaction (*cf.* ref. 16). The electron-releasing effect of the carbonyl-oxygen atom (*cf.* ref. 7) which is collinear with the  $S-O(\text{alkoxy})$  bond gives some 'unsymmetrical spiro- $\lambda^4$ -sulfane character' to the cyclic

alkoxysulfonium salts of this type, which may be illustrated by a minor contribution of the limiting hypervalent structures **4A** and **6A**.



(vi) The molecules **3–6** generally show butterfly-like shapes. The five-membered spiro-rings exhibit flattened envelope conformations, whereas the six-membered spiro-rings assume more or less inverted half-chair forms.

(vii) The bond systems in axial O–S–O moieties are practically unaffected by the size of the spiro-rings. Only the S···O interaction was found to be somewhat weaker in six-membered rings.

## Experimental

### General

Melting points were determined on a Boëtius 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 the Department of Organic Chemistry by Dr H. Medzihradsky-Schweiger and her co-workers.

Solvents were purified and dried by the usual methods; pyridine by distillation over P<sub>2</sub>O<sub>5</sub>. Evaporations were carried out under reduced pressure. Products obtained were dried *in vacuo* over P<sub>2</sub>O<sub>5</sub> or KOH pellets, depending on the solvent used.

### Materials

**Spiro[3H-2,1-benzoxathiole-1,1'-naphtho[1,8-d,e]-3H-2,1-oxathiin]-3-one (3).** Path (i) in Scheme 1. To a solution of 2-[8-(hydroxymethyl)-1-naphthylthio]benzoic acid<sup>8</sup> (**7**; 0.19 g, 0.6 mmol) in dry pyridine (2 cm<sup>3</sup>) was added dichloramine-T (TsNCl<sub>2</sub>; 0.084 g, 0.35 mmol; Ts = *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>) at room temp. The following day the white crystals of **3** were filtered off, washed with diethyl ether then dried (0.173 g, 91%), mp 226–228 °C (Found: C, 70.0; H, 3.9; O, 15.5; S, 10.5. C<sub>18</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 70.11; H, 3.92; O, 15.57; S, 10.40%);  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 1653vs (C=O);  $\delta_{\text{H}}$ (80 MHz; CDCl<sub>3</sub>; SiMe<sub>4</sub>) 5.72 (2 H, q, *J* 15, CH<sub>2</sub>), 7.5–8.5 (10 H, m, ArH).

**Spiro[3H-2,1-benzoxathiole-1,1'-naphtho[1,8-d,e]-3H-2,1-oxathiin]-3'-one (5).** Path (ii) in Scheme 1. A mixture of 8-iodo-1-naphthoic acid<sup>10</sup> (**8**; 52.2 g, 0.175 mol), 2-mercaptobenzyl alcohol<sup>11</sup> (**9**; 24.5 g, 0.175 mol), Cu<sub>2</sub>O (12.5 g, 0.0875 mol) and dry pyridine (260 cm<sup>3</sup>) was refluxed for 2 h under N<sub>2</sub> and after cooling to room temp. was poured into a mixture of ice (500 g) and concentrated aqueous HCl (500 cm<sup>3</sup>). The precipitate was filtered off, washed with water, then heated with a solution of NaOH (17.5 g) in water (350 cm<sup>3</sup>) at 100 °C for 1 h. After filtration, the filtrate was cooled and acidified (pH 1) with concentrated aqueous HCl. The crude 8-[2-(hydroxymethyl)-1-phenylthio]-1-naphthoic acid (**10**) was filtered off, washed with water and dried (48.8 g, 90%), mp 214–218 °C (EtOH) (Found: C, 69.4; H, 4.6; O, 15.3; S, 10.2. C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>S requires C, 69.65; H, 4.55; O, 15.46; S, 10.33%);  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3450–2300br (OH), 1685vs (C=O);  $\delta_{\text{H}}$ (80 MHz; (CD<sub>3</sub>)<sub>2</sub>SO; SiMe<sub>4</sub>) 4.39 (2 H, s, CH<sub>2</sub>), 6.8–8.6 (10 H, m, ArH).

**Path (iii) in Scheme 1.** The sulfide **10** (9.3 g, 0.03 mol) was dissolved in a solution of KHCO<sub>3</sub> (4 g, 0.04 mol) in water

(200 cm<sup>3</sup>) by heating on a steam bath, then chloramine-T (TsNClNa·3H<sub>2</sub>O; 9.3 g, 0.033 mol) was added and heated (100 °C) for 1 h. After cooling to room temp. the precipitate (TsNH<sub>2</sub>) was filtered off, the filtrate extracted with EtOAc (3 × 50 cm<sup>3</sup>) and then acidified (pH 1) with concentrated aqueous HCl. The precipitate was filtered off, washed with water and dried to give 8-[2-(hydroxymethyl)-1-phenylsulfinyl]-1-naphthoic acid (**11**; 8.2 g, 84%), mp 189–192 °C (EtOH–H<sub>2</sub>O) (Found: C, 66.1; H, 4.3; O, 19.6; S, 9.9. C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>S requires C, 66.14; H, 4.32; O, 19.63; S, 9.82%);  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3300–2200br (OH), 1673vs (C=O), 981s (S=O);  $\delta_{\text{H}}$ (80 MHz; (CD<sub>3</sub>)<sub>2</sub>SO; SiMe<sub>4</sub>) 4.26 (2 H, q, *J* 15, CH<sub>2</sub>), 7.2–8.3 (10 H, m, ArH).

**Path (iv) in Scheme 1.** To a solution of sulfoxide **11** (0.1 g, 0.3 mmol) in water-free dioxane (5 cm<sup>3</sup>) was added dicyclohexylcarbodiimide (0.068 g, 0.33 mmol) in water free dioxane (2 cm<sup>3</sup>) and stirred at room temp. for 1 h, then the precipitate (dicyclohexylurea) was filtered off. On addition of light petroleum (15 cm<sup>3</sup>) to the filtrate the crystals of the spiro- $\lambda^4$ -sulfane **5** that separated were filtered off, washed with diethyl ether and dried (0.04 g, 44%). Mp 146–166 °C (Found: C, 70.0; H, 3.9; O, 15.5; S, 10.5. C<sub>18</sub>H<sub>12</sub>O<sub>3</sub>S requires C, 70.11; H, 3.92; O, 15.57; S, 10.40%);  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 1625vs (C=O);  $\delta_{\text{H}}$ (80 MHz; CDCl<sub>3</sub>; SiMe<sub>4</sub>) 5.23 (2 H, s, CH<sub>2</sub>), 7.1–8.8 (10 H, m, ArH).

**1-[2'-(*N*-methylcarbamoyl)phenyl]-3H-2,1-naphtho[1,8-d,e]-oxathiin-1-ium chloride (4).** Compound **4** was prepared from *N*-methyl-2-[8-(hydroxymethyl)-1-naphthylthio]benzamide<sup>8</sup> by the procedure given in ref. 6, which is similar to that described for **14**; see path (ii) in Scheme 2. Mp 132–138 °C;  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3100–2600br (NH), 1625vs (C=O);  $\delta_{\text{H}}$ (60 MHz; CDCl<sub>3</sub>; SiMe<sub>4</sub>) 3.20 (3 H, d, *J* 4.5, Me), 6.0 (2 H, q, *J* 15.5, CH<sub>2</sub>), 7.4–8.3 (10 H, m, ArH).

**1-[8'-(*N*-methylcarbamoyl)-1'-naphthyl]-3H-2,1-benzoxathiol-1-ium perchlorate (6).** Path (i) in Scheme 2. A mixture of *N*-methyl-8-iodo-1-naphthamide<sup>8</sup> (**12**; 53.1 g, 0.17 mol), 2-mercaptobenzyl alcohol<sup>11</sup> (**9**; 23.9 g, 0.17 mol), Cu<sub>2</sub>O (12.2 g, 0.085 mol) and dry pyridine (300 cm<sup>3</sup>) was refluxed for 2 h under N<sub>2</sub>. After cooling to room temp., ice (1 kg) and concentrated aqueous HCl (600 cm<sup>3</sup>) was added to the mixture. The precipitate was filtered off, washed with water, dried, then extracted in a Soxhlet apparatus with EtOH (300 cm<sup>3</sup>). The EtOH solution of the product was evaporated to give a solid residue which was crystallized from pyridine–water to yield pure *N*-methyl-8-[2-(hydroxymethyl)-1-phenylthio]-1-naphthamide (**13**; 33.0 g, 60%). Mp 205–207 °C (Found: C, 70.5; H, 5.3; N, 4.3; O, 9.9; S, 9.8. C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub>S requires C, 70.56; H, 5.30; N, 4.33; O, 9.89; S, 9.91%);  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3300s (NH), 1617vs (C=O);  $\delta_{\text{H}}$ (80 MHz; (CD<sub>3</sub>)<sub>2</sub>SO; SiMe<sub>4</sub>) 2.79 (3 H, d, *J* 5, Me), 4.40 (2 H, d, *J* 6, CH<sub>2</sub>), 5.16 (1 H, t, *J* 6, OH), 6.9–8.2 (10 H, m, ArH).

**Path (ii) in Scheme 2.** To a suspension of sulfide **13** (6.5 g, 0.02 mol) in dry CH<sub>2</sub>Cl<sub>2</sub> (200 cm<sup>3</sup>), Bu<sup>t</sup>OCl (2.5 cm<sup>3</sup>, 0.02 mol) was added dropwise at room temp. under stirring. After further stirring (2 h) the solvent was removed. IR and <sup>1</sup>H NMR spectra showed that the solid residue (7.3 g, mp 70–118 °C) was an isomeric mixture of 1-[2'-(hydroxymethyl)phenyl]-2-methyl-3-oxo-3H-1,2-naphtho[1,8-d,e]thiazin-1-ium chloride (**15**; major product) and 1-[8'-(*N*-methylcarbamoyl)-1'-naphthyl]-3H-2,1-benzoxathiol-1-ium chloride (**14**; minor product; ≤ 5%). For this mixture:  $\nu_{\max}/\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>) 3600w (OH), 3440w (NH), 1694vs, 1665sh (C=O);  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>; SiMe<sub>4</sub>) 3.78 (3 H, s, Me), 5.22 (2 H, q, *J* 15.5, CH<sub>2</sub>), 7.27–9.26 (10 H, m, ArH).

The crude mixture was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (70 cm<sup>3</sup>) and pentane (10 cm<sup>3</sup>) was added dropwise. Next day the crystals that had separated were filtered off, washed with cold solvent and diethyl ether, then dried (1.15 g, 16%). Mp 128–132 °C (Found: C, 63.0; H, 4.4; Cl, 9.6; N, 4.0; O, 8.8; S, 8.9.

**Table 5** X-Ray crystallographic data for spiro- $\lambda^4$ -sulfanes and analogous sulfonium salts **3–6**

Compound	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>18</sub> H <sub>12</sub> O <sub>3</sub> S	C <sub>19</sub> H <sub>16</sub> ClNO <sub>2</sub> S·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>18</sub> H <sub>12</sub> O <sub>3</sub> S·1/2C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	C <sub>19</sub> H <sub>16</sub> ClNO <sub>6</sub> S
Molecular mass	308.36	442.76	352.39	421.84
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	Cc	P $\bar{1}$	P $\bar{1}$	P2 <sub>1</sub> /c
<i>a</i> /Å	21.904(1)	9.891(1)	8.704(1)	11.078(1)
<i>b</i> /Å	8.270(1)	11.158(1)	9.265(1)	12.216(2)
<i>c</i> /Å	7.821(1)	12.279(1)	10.914(1)	13.775(2)
<i>a</i> <sup>o</sup>	90	56.84(1)	71.76(1)	90
<i>β</i> <sup>o</sup>	102.76(1)	61.94(1)	85.89(1)	97.10(1)
<i>γ</i> <sup>o</sup>	90	72.11(1)	73.54(1)	90
Cell volume/Å <sup>3</sup>	1381.8(5)	998.8(2)	801.5(2)	1849.9(4)
<i>Z</i>	4	2	2	4
<i>F</i> (000)	640	456	368	872
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.480	1.472	1.460	1.515
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan rate °min <sup>-1</sup>	1–20	1–20	1–20	1–20
Scan width	0.50 + 0.14 tan $\theta$	0.45 + 0.14 tan $\theta$	0.50 + 0.14 tan $\theta$	0.50 + 0.14 tan $\theta$
X-Ray radiation	Cu-K $\alpha$	Cu-K $\alpha$	Cu-K $\alpha$	Cu-K $\alpha$
$\lambda$ /Å	1.54184	1.54180	1.54180	1.54180
$\mu$ /mm <sup>-1</sup>	2.173	5.262	1.995	3.227
Crystal size (mm)	0.18 × 0.25 × 0.30	0.17 × 0.20 × 0.25	0.30 × 0.20 × 0.15	0.15 × 0.35 × 0.35
$\theta$ Range (°)	1.5–75.0	1.5–75.0	4.2–75.0	4.0–75.5
Total reflections	1571	4091	3296	4210
Non-zero reflections	1423	3419	2892	2993
Number of Reflections used in Refinement	1408	4091	2892	3829
Parameters refined	199	246	227	268 disordered ClO <sub>4</sub> <sup>-</sup> ion
Refinement on $\sigma$ level	<i>F</i> <sup>2</sup> 3.0	<i>F</i> <sup>2</sup> 3.0	<i>F</i> <sup>2</sup> 2.0	<i>F</i> <sup>2</sup> 2.0
Weighting scheme	1/[ $\sigma^2(F_o)^2 + (0.0456P)^2 + 4.0422P$ ] <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	1/[ $\sigma^2(F_o)^2 + (0.0922P)^2 + 0.1375P$ ] <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	1/[ $\sigma^2(F_o)^2 + (0.0739P)^2 + 0.1700P$ ] <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	1/[ $\sigma^2(F_o)^2 + (0.1405P)^2 + 0.8642P$ ] <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
$R = \Sigma \Delta F / \Sigma F_o$	0.028	0.078	0.040	0.072
$R = \Sigma w(\Delta F^2) / \Sigma  F_o ^2$	0.069	0.100	0.114	0.196
$S = \Sigma (w F_o  -  F_c )^2 / (N_o - P)^{1/2}$	0.66	1.07	1.08	1.052
Max. LS shift to Error ratio ( $\Delta/\sigma$ )	0.02	0.55	0.02	0.01
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	0.19	0.75	0.40	0.710
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.34	-0.51	-0.31	-0.753

C<sub>19</sub>H<sub>16</sub>ClNO<sub>2</sub>S requires C, 63.77; H, 4.51; Cl, 9.91; O, 8.94; N, 3.91; S, 8.96%; the IR and <sup>1</sup>H NMR spectra were identical to those ones obtained for the crude product indicating that crystallization did not affect the ratio of the isomers **14** and **15**.

**Path (iii) in Scheme 2.** To the solution of sulfonium chlorides **14** and **15** obtained by crystallization (2.37 g, 0.01 mol) in dry MeOH (150 cm<sup>3</sup>) was added AgClO<sub>4</sub> (2.01 g, 0.01 mol) in dry MeOH (20 cm<sup>3</sup>) under stirring at room temp. After further stirring (2 h) the precipitate (AgCl) was filtered off and the filtrate allowed to stand for 3 d. Some crystals of the alkoxysulfonium perchlorate **6** separated, which were sufficient only for the X-ray crystal structure determination and for obtaining IR and <sup>1</sup>H NMR spectra. Mp 175–205 °C;  $\nu_{\max}/\text{cm}^{-1}$  (KBr) 3300m (NH), 1622vs (C=O), 1100vs, 618s (ClO<sub>4</sub>);  $\delta_{\text{H}}$ (80 MHz, (CD<sub>3</sub>)<sub>2</sub>SO; SiMe<sub>4</sub>) 3.55 (3 H, s, Me), 5.05 (2 H, d, *J*13, CH<sub>2</sub>), 7.3–8.9 (10 H, m, ArH).

**Path (iv) in Scheme 2.** The acylaminosulfonium compound **15** was identified by means of its cuprous complex salt (**16**). To the mixture of **14** and **15** (*vide supra*) dissolved in dry methanol was added a solution of CuCl<sub>2</sub> in dry methanol to give the complex salt **16** in quantitative yield. After crystallization from dry methanol we could get X-ray-quality single crystals of **16** and its molecular structure was determined by X-ray diffraction. The details of the latter investigations together with the determination of the molecular structures of other sulfonium salts with CuCl<sub>4</sub><sup>-</sup> complex anion will be published elsewhere.

### Structure analysis and refinements

X-Ray-quality single crystals were grown from pyridine for **3**, from a solvent mixture of EtOH–CH<sub>2</sub>Cl<sub>2</sub> and diethyl ether for **4**, from dioxane–diethyl ether solvent mixture for **5** and methanol for **6**. Table 5 summarizes the relevant data concerning the crystal structure analyses. Each data set was collected at room temp. on a CAD-4 diffractometer equipped with graphite monochromator.

Lattice parameters were refined by least-squares fit for 25 reflections. Standard reflections (three for each data collection) indicated no decay of the crystals. All reflections were corrected for Lorenz and polarization effects.<sup>20,21</sup> No absorption corrections were applied.

The crystallographic phase problems were solved by direct methods using the MULTANE82 program<sup>22</sup> for **3–5** and the SHELXS(86) program<sup>23</sup> for **6**. The atomic positions for each structure were refined with anisotropic displacement parameters in *F*<sup>2</sup> mode using the SHELXL(93) program.<sup>24</sup> (Preliminary reports on **3**, **4** and **5** published earlier<sup>6,15</sup> are based on least-squares refinements on *F*). The hydrogen positions were generated from assumed geometries and refined isotropically in riding mode. A dioxane molecule on a centre of symmetry was found in a difference map of **5** and refined adequately together with the spiro- $\lambda^4$ -sulfane molecule. Similarly, a guest molecule CH<sub>2</sub>Cl<sub>2</sub> could be located and refined in **4**. In contrast, in **6** the O atoms of the tetrahedral ClO<sub>4</sub><sup>-</sup> show positional disorder. From



difference maps, three sets distinguished and were subsequently refined (one of them is shown in Fig. 4).

Fractional atomic coordinates, bond lengths and angles as well as thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.¶

### Acknowledgements

This work was supported by the Hungarian Scientific Research Foundation (OTKA, No. T017187). The authors thank Professor Árpád Kucsman for the fruitful discussions to find the final form of the manuscript.

¶ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/63.

### References

- 1 L. J. Adzima, E. N. Duesler and J. C. Martin, *J. Org. Chem.*, 1977, **42**, 4001.
- 2 P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, 1977, **99**, 5761.
- 3 W. Y. Lam, E. N. Duesler and J. C. Martin, *J. Am. Chem. Soc.*, 1981, **103**, 127.
- 4 D. Szabó, I. Kapovits, Á. Kucsman, P. Huszthy, Gy. Argay, M. Czugler, V. Fülöp, A. Kálmán, T. Koritsánszky and L. Párkányi, *J. Mol. Struct.*, 1993, **300**, 23.
- 5 D. Szabó, I. Kapovits, Á. Kucsman, V. Fülöp, M. Czugler and A. Kálmán, *Struct. Chem.*, 1990, **1**, 305.
- 6 D. Szabó, I. Kapovits, Á. Kucsman, M. Czugler, V. Fülöp and A. Kálmán, *Struct. Chem.*, 1991, **2**, 529.
- 7 J. G. Ángyán, R. A. Poirier, Á. Kucsman and I. G. Csizmadia, *J. Am. Chem. Soc.*, 1987, **109**, 2237.
- 8 D. Szabó and I. Kapovits, *Sulf. Lett.*, 1991, **13**, 37.
- 9 I. Kapovits, J. Rábai, F. Ruff and Á. Kucsman, *Tetrahedron*, 1979, **35**, 1869.
- 10 R. J. Bailey, P. J. Card and H. Schechter, *J. Am. Chem. Soc.*, 1983, **105**, 6096.
- 11 K. Pelz, I. Jirkovsky, E. Adlerova, J. Metysova and M. Protiva, *Collect. Czech. Chem. Commun.*, 1968, **33**, 1895.
- 12 Á. Kucsman, I. Kapovits and B. Tanács, *Tetrahedron*, 1962, **18**, 79.
- 13 I. Kapovits, J. Rábai, D. Szabó, K. Czákó, Á. Kucsman, Gy. Argay, V. Fülöp, A. Kálmán, T. Koritsánszky and L. Párkányi, *J. Chem. Soc., Perkin Trans. 2*, 1993, 847.
- 14 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960, 3rd edn., p. 221.
- 15 A. Kálmán, *Croat. Chem. Acta*, 1993, **66**, 519.
- 16 Á. Kucsman and I. Kapovits, in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, ed. F. Bernardi, I. G. Csizmadia and A. Mangini, Elsevier, Amsterdam, 1985, p. 185.
- 17 F. H. Allen, O. Kennard, D. G. Watson, L. Branner, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
- 18 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
- 19 R. Bucourt, *Top. Stereochem.*, 1974, **8**, 159.
- 20 Enraf-Nonius, SDP-Plus Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1983.
- 21 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.
- 22 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, MULTAN82, A System of Computer Programs for the Automatic Solution of Crystal Structures for X-ray Diffraction Data, Universities of York, England and Louvain, Belgium, 1982.
- 23 G. M. Sheldrick, SHELXS(86) *Acta Crystallogr., Sect. B*, 1990, **46**, 467.
- 24 G. M. Sheldrick, SHELXL(93) Program for Crystal Structure Refinement, University of Göttingen, Germany, 1994.

Paper 6/04157D  
Received 13th June 1996  
Accepted 15th January 1997