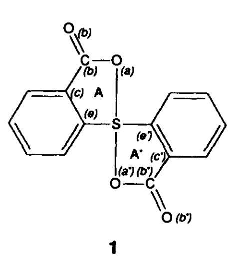
Diaryldiacyloxyspirosulfuranes. Part 3.[1] Sulfuranes with Five-, Six- and Seven-membered Spirorings: Syntheses and Molecular Structures

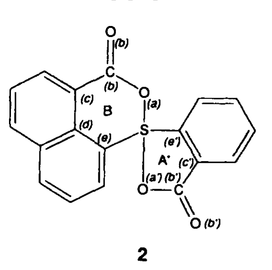
István Kapovits,[*,a] József Rábai,[a] Dénes Szabó,[a] Klára Czakó,[a] Árpád Kucsman,[a]
Gyula Argay,[b] Vilmos Fülöp,[b] Alajos Kálmán,[*,b] Tibor Koritsánszky[b] and
László Párkányi[b]
[a] *Department of Organic Chemistry, L. Eötvös University, H-1518 Budapest 112, PO Box 32, Hungary*
[b] *Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, PO Box 17, Hungary*

Three novel diaryldiacyloxyspirosulfuranes (**2**–**4**) with five-, six- and seven-membered spirorings have been prepared, and their molecular structures determined by X-ray diffraction. The structure of spirosulfurane **1** with two identical five-membered spirorings has been reinvestigated. In all spirosulfuranes **1**–**4** the arrangement of the ligands about the central sulfur atom show a slightly distorted trigonal bipyramidal (TBP) geometry resulting in chiral molecular structure. The axial (hypervalent) S–O and equatorial (covalent) S–C_{ar} bond lengths range from 1.838(1) to 1.872(3) and from 1.771(3) to 1.794(4) Å, respectively. The axial O–S–O and equatorial C_{ar}–S–C_{ar} bond angles lie in the narrow intervals of 174.9(2)–177.4(4)° and 105.8(2)–106.9(2)°, respectively. The five-membered spirorings are practically planar in **1**–**3**. The six-membered spirorings in **2** and **4** assume distorted sofa conformations. The seven-membered spiroring in **3**, having four C_{ar} atoms with planar configuration, is irregular. The aromatic rings fused with the spirorings are perpendicular to the equatorial plane only if the spiroring is five-membered. In other cases the stable conformations with TBP geometry about sulfur involve a significant torsion of the aromatic ring about the S–C_{ar} axis. Thus, in diaryldiacyloxyspirosulfuranes having acyloxy–O ligands at axial positions the structural parameters about the sulfur are not considerably influenced by the shape and size of the spirorings. The O–S–O moiety with hypervalent bonds may be regarded as a structural unity. The sum of the individual S–O bond lengths, (3.684–3.744 Å) which is characteristic of diaryldiacyloxyspirosulfuranes, differs markedly from the values found earlier for dialkoxy- and acyloxy-alkyloxy analogues (3.601 and 3.910 Å, respectively). For spirosulfurane **3** a rearrangement into the isomeric ten-membered cyclic anhydride **13** is observed.

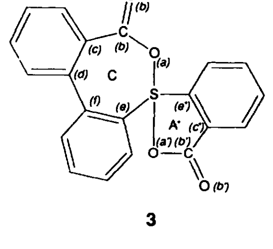
As a part of our investigations designed to establish correlations between molecular structures and chemical properties of spirosulfuranes, we prepared diaryldiacyloxyspirosulfuranes with five-, six- and seven-membered spirorings (**1**, **2**, **3** and **4**) and determined their molecular structures by X-ray diffraction. In view of this aim, kinetic measurements were also made for the hydrolysis of the prepared spirosulfuranes **1**–**4**, and the results are to be published in the following paper.[2]



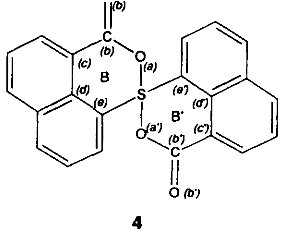
1



2



3



4

As the first representative of diaryldiacyloxyspirosulfuranes, the spirosulfurane **1** had been reported by us together with its synthesis[3] and molecular structure determination by X-ray diffraction.[4] In subsequent publications we reported both on the syntheses and spectroscopic (UV, IR) data of the derivatives of **1** having five-membered spirorings and differently substituted benzene rings, as well as on the mechanisms of their formations and hydrolyses investigated by preparative methods.[1,5]

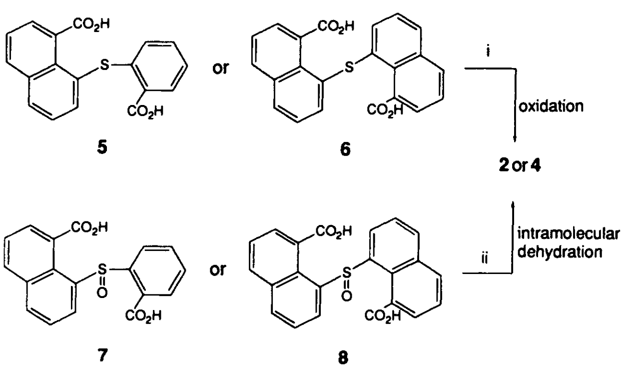
The molecular structure of spirosulfurane **1**, similarly to other sulfuranes,[6] exhibits a slightly distorted trigonal bipyramidal (TBP) geometry about the central sulfur atom, where the more electronegative acyloxy ligands are in the axial positions with the two aryl carbons and the lone pair in the equatorial ones. The axial S–O bonds (1.82 Å) were found[4] to be considerably longer than the sum of the sulfur and oxygen covalent radii[7] (1.70 Å). The axial O–S–O angle (178.5°) was near to the ideal 180°. The structural data determined in **1** and in other sulfuranes[6] substituted symmetrically in axial positions can be well interpreted on the basis of Musher's theory[6,8] assuming hypervalent three-centre four-electron bonds in the axial array.

In this paper we describe the syntheses and molecular structures of three novel diaryldiacyloxyspirosulfuranes in which the five-membered spirorings of **1** (A and A' rings) are partly (**2** and **3**) or fully (**4**) replaced by six- or seven-membered rings (B, B' and C rings, respectively). The structure of spirosulfurane **1** has also been reinvestigated with refining on new diffractometer data collected with Mo-Kα radiation.

In addition to the comparison of structural parameters, another point also prompted us to study the effect of changing the size of spirorings in spirosulfuranes, that is the five-membered ring effect, known to stabilize the 10-P-5 and 10-S-4 hypervalent species.[6] Since the spirosulfuranes **1**–**4** can be classified as 10-S-4 species, they seem to be appropriate models for studying the efficiency of the ring effect by comparing their molecular structures and resistance to hydrolysis.[2]

Results and Discussion

Syntheses.—The syntheses for spirosulfuranes **2** and **4** were based on known methods (i and ii in Scheme 1) described for **1** in earlier publications.[1,5] In path i the sulfide **5** or **6** was oxidized with the halogenating agent dichloramine-T in dry pyridine solvent resulting in spirosulfurane **2** or **4**. Starting from the sulfoxide **7** or **8** (path ii), the intramolecular dehydration was carried out with acetic anhydride in dry pyridine solvent to give the corresponding spirosulfurane **2** or **4**.

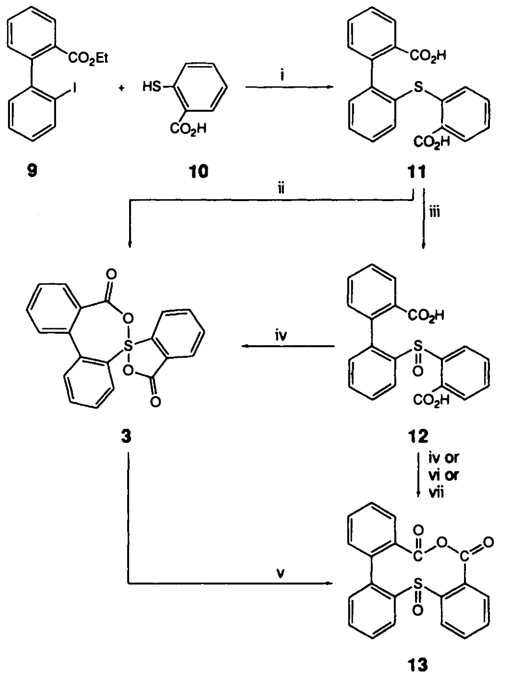


Scheme 1

In the synthesis of the spirosulfurane **3** (Scheme 2), ethyl 2-iodobiphenyl-2′-carboxylate (**9**)[9] was first coupled with thiosalicylic acid (**10**; path i), and the corresponding sulfide **11** was oxidized directly to the spirosulfurane **3** with iodobenzene diacetate (path ii; *cf.* ref 5). The spirosulfurane precursor sulfoxide **12** was prepared by the oxidation of sulfide **11** with phenyltrimethylammonium tribromide (PTAB)[10] in aqueous pyridine solution (path iii). When sulfoxide **12** was treated with acetic anhydride in dry pyridine (path iv), after heating for a short time at 100 °C, a mixture of spirosulfurane **3** and cyclic anhydride **13** could be isolated.* On the other hand, the spirosulfurane **3** obtained by the direct method (path ii) could be transformed into the cyclic anhydride **13** by heating in dry pyridine (path v). These latter experimental observations suggest that the formation of cyclic anhydride **13** proceeds through the spirosulfurane **3**. The formation of cyclic anhydride **13** was observed exclusively when the experimental conditions of the intramolecular dehydration were altered (path vi, vii).

Crystallographic Analyses.—The molecular structures for spirosulfuranes **1**–**4** were determined by single crystal X-ray diffraction methods. The stereoscopic views are shown in Figs. 1–4.

Sulfur Configuration.—Like compound **1**, the spirosulfuranes **2**–**4** show slightly distorted trigonal bipyramidal (TBP) geometry about the sulfur atom with electronegative acyloxy-oxygens (O_a and $O_{a'}$) in the axial positions and with aryl carbons (C_e and $C_{e'}$) in the equatorial positions (see **1**–**4** and Figs. 1–4). This means that the TBP geometry of spirosulfuranes is not remarkably influenced either by the size of the spirorings or by aromatic rings fused onto the spirorings. On the other hand, the most favourable conformations of the spirosulfurane skeleton are controlled by other steric factors *e.g.* (i) by the actual position of the axial oxygens, (ii) by the shape of the spirorings and (iii) by the relative position of the condensed aromatic ring, as will be discussed later.

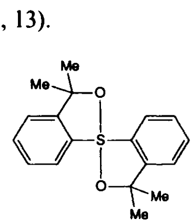


Scheme 2 *Reagents and conditions:* i, Cu_2O, pyridine, reflux, 2 h, then hydrolysis with NaOH; ii, $PhI(OAc)_2$, AcOH, 30–40 °C, 12 h; iii, PTAB, pyridine–water, 20 °C, 1 h; iv, Ac_2O, pyridine, 100 °C; v, pyridine, 100 °C, 30 min; vi, Ac_2O, AcOH, 118 °C, 5 min; vii, AcCl, TEA, DMF, 25 °C, 5 min.

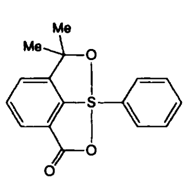
The molecules of all four spirosulfuranes **1**–**4** are chiral. The spiro compounds **1** and **4** exhibit C_2 molecular symmetry, while the derivatives **2** and **3** are asymmetric.

Bond Lengths and Angles about the Central Sulfur.—Selected bond lengths, bond angles and torsion angles characteristic of the spirosulfuranes **1**–**4** are listed in Table 1.

The S–C_e and S–$C_{e'}$ bond lengths (1.794–1.771 Å) in the equatorial plane are similar to the average values obtained for aryl sulfoxides (S^{IV}–C_{ar} 1.790 Å) and aryl sulfones (S^{VI}–C_{ar} 1.763 Å).[12] As expected, the axial S–O_a distances (1.842–1.872 Å) related to hypervalent bonds are much longer than the sum of the sulfur and oxygen covalent radii (1.70 Å).[7] The individual values found for S–O bonds in **1**–**4** do not differ markedly from one another and cannot be well correlated with the size of the spirorings. Nevertheless, the sum of the S–O_a and S–$O_{a'}$ bond lengths, *i.e.* the O_a–S–$O_{a'}$ distance (3.684–3.744 Å for **1**–**4**) is characteristic of these spirosulfurane systems. For example, this distance in diaryldiacyloxyspirosulfurane **1** (3.684 Å) is considerably longer than in the analogous dialkoxy compound **14**, but shorter than in the mixed acyloxy-alkoxy compound **15** (3.601 and 3.910 Å,[13] respectively). This phenomenon can be attributed to the different electronegativities of the axial ligands (*cf.* refs. 8, 13).



14



15

The gradual increase of O_a–S–$O_{a'}$ distances in spirosulfuranes **1**–**4** is accompanied by a similar decrease of O_a–S–$O_{a'}$ bond angles and S–C_e bond lengths. These changes may be ascribed to a slight deformation toward a sulfone-like configuration.

---

* It was only the first time, that the spirosulfurane **3** crystallized from the reaction mixture on addition of ether (yield 35%), probably due to the absence of seeds of **13** in the laboratory. The molecular structure of **13** was determined by an X-ray method.[11]

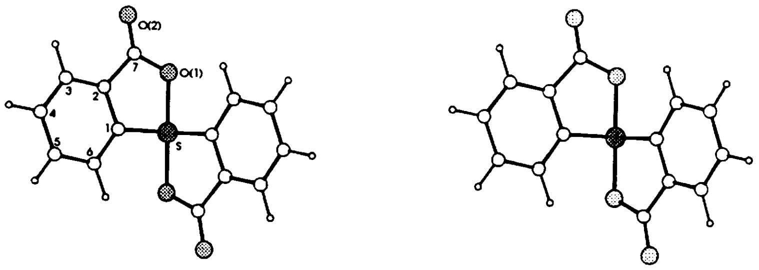


Fig. 1 Stereoscopic view of spirosulfurane **1** with numbering scheme for nonhydrogen atoms

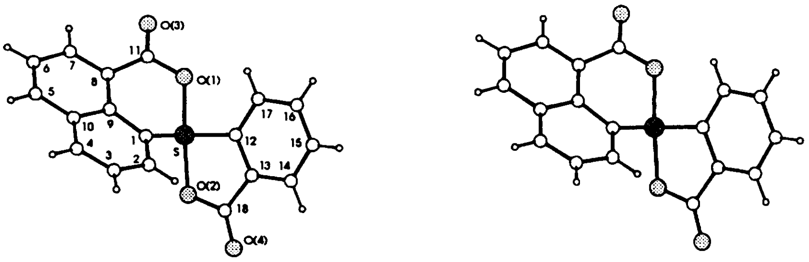


Fig. 2 Stereoscopic view of spirosulfurane **2** with numbering scheme for nonhydrogen atoms

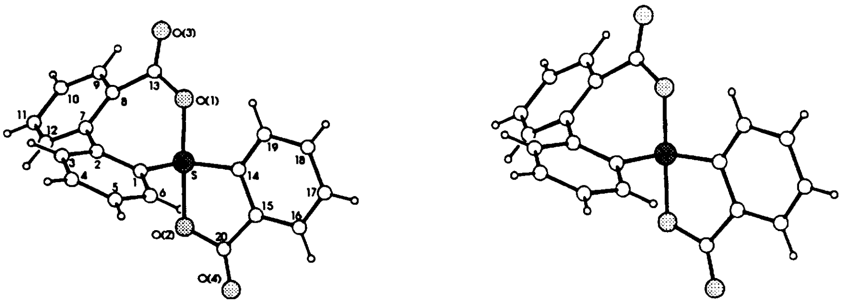


Fig. 3 Stereoscopic view of spirosulfurane **3** with numbering scheme for nonhydrogen atoms

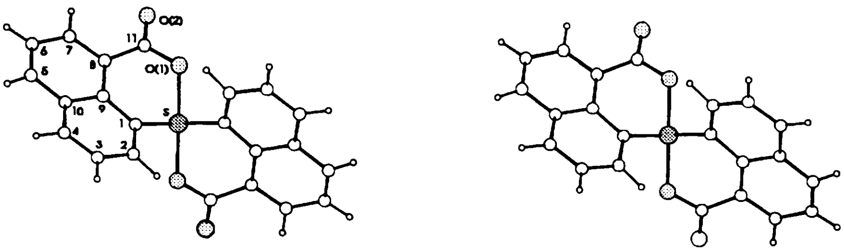


Fig. 4 Stereoscopic view of spirosulfurane **4** with numbering scheme for nonhydrogen atoms

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

	Spirosulfuranes[a]			
	1[b]	**2**	**3**	**4**[b]
Bond lengths (Å)				
S–O_a	1.842(3)	1.838(1)	1.857(3)	1.872(3)
S–O_a	1.842(3)	1.869(2)	1.862(3)	1.872(3)
S–C_e	1.794(5)	1.789(2)	1.784(4)	1.771(3)
S–$C_{e'}$	1.794(5)	1.794(2)	1.786(4)	1.771(3)
C_b–O_a	1.320(9)	1.334(2)	1.342(5)	1.346(4)
$C_{b'}$–$O_{a'}$	1.320(9)	1.333(3)	1.334(5)	1.346(4)
C_b–O_b	1.192(8)	1.210(3)	1.208(6)	1.202(5)
$C_{b'}$–$O_{b'}$	1.192(8)	1.205(3)	1.207(6)	1.202(5)
Bond angles (°)				
O_a–S–$O_{a'}$	177.7(4)	176.7(1)	175.7(2)	174.9(2)
C_e–S–$C_{e'}$	106.9(4)	105.8(2)	105.9(3)	106.9(2)
O_a–S–$C_{e'}$	91.3(4)	90.8(1)	89.8(3)	90.0(2)
$O_{a'}$–S–C_e	91.3(4)	90.7(1)	89.3(3)	90.0(2)
Torsion angles (°)				
S–O_a–C_b–O_b	−173(2)	−147.2(4)	−159(1)	−138.5(8)
S–$O_{a'}$–$C_{b'}$–$O_{b'}$	−173(2)	−173.3(5)	−174.1(1)	−138.5(8)
O_a–S–$C_{e'}$–$C_{e'/d'}$	−177(1)	−176.8(3)	−178.8(7)	−136.4(4)
$O_{a'}$–S–C_e–$C_{c/d/f}$	−177(1)	−135.4(3)	−114.1(6)	−136.4(4)
C_e–S–$C_{e'}$–$C_{c'}$	95.5(9)	90.7(3)	92.9(6)	−130.4(4)
$C_{e'}$–S–C_e–$C_{c/d/f}$	95.5(9)	137.5(2)	158.8(6)	−130.4(4)

[a] Atoms are signed with lettering in the lower indices according to formulae **1**–**4**. [b] Equal values related to C_2 molecular symmetry.

Table 2 Endocyclic bond angles (°) pertaining to the spirorings with e.s.d.s in parentheses

	Spirosulfuranes[a]			
	1	**2**	**3**	**4**
Spirorings	A	B	C	B=B′
C_e–S–O_a	87.3(4)	92.2(1)	88.4(3)	93.1(2)
S–O_a–C_b	115.2(8)	119.4(2)	116.5(4)	117.6(4)
O_a–C_b–C_c	111(1)	116.8(3)	118.8(6)	115.5(5)
C_b–C_c–C_e	114(1)	—	—	—
C_c–C_e–S	112.5(8)	—	—	—
C_b–C_c–C_d	—	121.0(3)	124.0(6)	121.9(5)
C_c–C_d–C_e	—	124.2(3)	—	124.7(5)
C_d–C_e–S	—	116.3(3)	—	118.0(4)
C_c–C_d–C_f	—	—	124.4(6)	—
C_d–C_f–C_e	—	—	122.6(6)	—
C_f–C_e–S	—	—	114.9(5)	—
Spirorings	A′	A′	A′	
$C_{e'}$–S–$O_{a'}$	87.3(4)	87.0(1)	87.4(3)	
S–$O_{a'}$–$C_{b'}$	115.2(8)	114.9(2)	114.8(5)	
$O_{a'}$–$C_{b'}$–$C_{c'}$	111(1)	109.9(3)	110.2(6)	
$C_{b'}$–$C_{c'}$–$C_{e'}$	114(1)	115.2(3)	114.7(7)	
$C_{c'}$–$C_{e'}$–S	112.5(8)	112.7(3)	112.6(5)	

[a] Atoms are signed with lettering in the lower indices according to formulae **1**–**4**

Table 3 Endocyclic torsion angles (°) pertaining to the spirorings with e.s.d.s in parentheses

	Spirosulfuranes[a]			
	1	**2**	**3**	**4**
Spirorings	A	B	C	B=B′
O_a–S–C_e–C_c	5.07(7)	—	—	—
C_b–O_a–S–C_e	−5.5(8)	−59.9(3)	−91.1(5)	−60.7(5)
C_c–C_b–O_a–S	4.3(5)	39.0(2)	22.2(4)	46.7(4)
C_e–C_c–C_b–O_a	0(1)	—	—	—
S–C_e–C_c–C_b	−3.8(7)	—	—	—
O_a–S–C_e–C_d	—	46.1(2)	—	39.5(4)
C_d–C_c–C_b–O_a	—	4.2(3)	39.4(7)	−4.4(6)
C_e–C_d–C_c–C_b	—	−15.0(3)	—	−15.5(6)
S–C_e–C_d–C_c	—	−18.8(3)	—	−10.8(4)
O_a–S–C_e–C_f	—	—	69.5(5)	—
C_f–C_d–C_c–C_b	—	—	−3.3(7)	—
C_e–C_f–C_d–C_c	—	—	−52.6(7)	—
S–C_e–C_f–C_d	—	—	4.6(5)	—
Spirorings	A′	A′	A′	
$O_{a'}$–S–$C_{e'}$–$C_{c'}$	5.07(7)	0.8(2)	4.4(5)	
$C_{b'}$–$O_{a'}$–S–$C_{e'}$	−5.5(8)	−4.1(3)	−4.8(5)	
$C_{c'}$–$C_{b'}$–$O_{a'}$–S	4.3(5)	5.9(2)	3.7(3)	
$C_{e'}$–$C_{c'}$–$C_{b'}$–$O_{a'}$	0(1)	−5.3(3)	−0.3(6)	
S–$C_{e'}$–$C_{c'}$–$C_{b'}$	3.8(7)	2.3(2)	−3.4(4)	

[a] Atoms are signed with lettering in the lower indices according to formulae **1**–**4**.

Owing to the TBP geometry, all of the O–S–C_{ar} bond angles in **1**–**4** are near 90° and the O–S–O moieties are almost linear. In most cases the S–O bonds are slightly bent toward the aromatic rings (the endocyclic O–S–C bond angles are usually somewhat smaller than 90°). In compound **4** with endocyclic O–S–C bond angles of 93° both S–O bonds are inclined toward the sulfur lone pair, meaning that the O–S–O bond angle is 185.1(2)° rather than 174.9(2)° as given in Table 1.

Conformations of Spirosulfurane Rings.—Endocyclic bond and torsion angles for the five- (A and A′), six- (B and B′) and seven-membered (C) spirorings are listed in Tables 2 and 3.

The five-membered rings (A and A′) in all of spirosulfuranes **1**–**4** are planar, within experimental error, with endocyclic torsion angles (φ) smaller than 5°. The fusion of the planar spirorings (A and A′) with benzene rings does not cause any steric strain. The aromatic rings are nearly perpendicular to the equatorial plane as shown by the $C_{e'}$–S–C_e–C_c torsion angles of 90–95°.

The six-membered rings (B and B′) in both the asymmetric sulfurane **2**(φ = −15°, +4°, +39°, −60°, +46°, −19°) and the symmetric sulfurane **4**(φ = −15°, +4°, +47°, −61°, +40°,

$-11°$) assume a distorted sofa conformation with the S atom on the flap. The shape of the spirorings may be compared to that accepted for the sofa form of cyclohexene ($\varphi = -11°, 0°, +32°, -58°, +57°, -20°$, *cf.* ref. 14). The puckering parameters[15] are for **2** and **4**: $Q = 0.622(2)$ and $0.597(6)$ Å, $\Phi = 9.8(2)°$ and $21.2(6)°$, $\Theta = 61.4(2)°$ and $60.2(5)°$, respectively, if the atomic numbering in the calculations starts from S through O(1), *etc.* The fusion of the six-membered non-planar spirorings (B and B′) with the naphthalene ring in the 1,8-positions is associated with a slight torsion of the parallel 'amphi' valence directions. In addition, the plane of the naphthalene ring is no longer perpendicular to the equatorial plane: the $C_{e'}$–S–C_e–C_d torsion angles are between 130 and 137°.

The seven-membered spiroring (C) in compound **3** fused with a biphenyl ring in the 2,2′-positions, has two planar regions, owing to the four C_{ar} ring atoms. Therefore the 'irregular' conformation observed cannot be compared to the typical stable conformations of cycloheptane.[16] The unhindered rotation about the C_{ar}–C_{ar} axis of the biphenyl part with the actual torsion angle of 50.9° allows the C spiroring to assume a strain-free conformation maintaining the regular TBP geometry about sulfur. Resembling the six-membered rings, the maximum torsion angle in the C ring occurs about the S–O_a axis, indicating that the sulfur atom is raised markedly above the 'average plane' of the ring. The $C_{e'}$–S–C_e–C_f torsion angle of 159° reveals that one of the benzene rings in the biphenyl moiety is far from being perpendicular to the equatorial plane.

Crystal Structures.—The butterfly like molecules of the symmetrical spirosulfuranes **1** and **4** retain their C_2 molecular symmetry in the crystal structures formed equally with the space group *Fdd* 2 (No. 43). Both are sitting on the twofold axes parallel with the rather short *c* parameters. These two structures, in terms of the isostructuralism, can be described as quasi-isostructural crystals (for classification see ref. 17). From their similar packing it equally follows that the central sulfur atoms do not form any close intermolecular contacts.

The asymmetric molecule of the spirosulfurane **2** located in a triclinic unit cell exhibits the shortest S···O close intermolecular contact of 3.291(1) Å indicating, however, only a weak interaction (the sum of the van der Waals radii[18] for S and O is 3.25 Å). Including the carbonyl oxygen O_b at ($-x$, $2-y$, $1-z$), the S···O close contact makes an angle of 145.18(7)° with the S–C_e bond of another molecule.

An even weaker intermolecular S···O close contact was revealed in the orthorhombic unit cell of the spirosulfurane **3**, in which a carbonyl oxygen O_b is coordinated to sulfur at a distance of 3.346(4) Å to the sulfur atom in a neighbouring molecule related by a centre of symmetry at (1/2, 0, 0). The orientation of the oxygen atom is also characterised by a nonlinear O_b···S–C_e angle of 143.0(2)°.

Conclusions

There are several synthetic routes for the preparations of symmetrically substituted diaryldiacyloxyspirosulfuranes with five-, six- and seven-membered spirorings (**1**–**4**) and for the rearrangement of the spirosulfurane **3** into a ten-membered cyclic anhydride (**13**). By X-ray structure determination we can compare the geometric parameters about sulfur characteristic of the molecular structures of sulfuranes, and explain how the size and shape of the spirorings influence these parameters. Thus, it may be concluded that (i) the structural parameters about sulfur in spirosulfuranes of S^{IV}[C,C,O,O] type with aromatic carbon and acyloxy-oxygen are close to one another and not considerably influenced by the shape and size of the spirorings; (ii) the individual axial S–O bond lengths cannot be correlated with the size of the spirorings, but the corresponding O–S–O distances increase gradually from **1** to **4**, parallel with the decrease of O–S–O bond angles and S–C_{ar} bond lengths. The O–S–O distances in diacyloxysulfuranes are longer than those in dialkoxy analogues, but shorter than in mixed alkoxy-acyloxy derivatives.

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. The EI and CI (isobutane) mass spectra for spirosulfurane **3** were recorded with MS 25-RFA instrument (direct evaporation at 260 °C); the EI and CI mass spectra for **1**, **2** and **4** had been published earlier[19] with the explanation of their fragmentation routes. Microanalyses were carried out in the microanalytical laboratory of this department by Dr. H. Medzihradszky-Schweiger and her co-workers.

Solvents were purified and dried by usual methods; pyridine by distillation over P_2O_5. The evaporations were carried out under reduced pressure. Products obtained from reaction mixtures or by crystallization were isolated in the following manner: after filtration and washing with cold solvent and diethyl ether, they were dried *in vacuo* over P_2O_5 or KOH pellets, depending on the solvent used.

Materials.—1,1′-*Spirobi*(3H-2,1-*benzoxathiole*)-3,3′-*dione* (**1**). The spirosulfurane **1** was prepared as described in ref. 1 starting from 2,2′-sulfinyldibenzoic acid which was dehydrated with Ac_2O in AcOH solvent.

3H-2,1-*Benzoxathiole*-1-*spiro*-1′-(3H-*naphtho*[1,8-d,e]-2,1-*oxathiine*)-3,3′-*dione* (**2**). (i) To a solution of 2-(8-carboxy-1-naphthylthio)benzoic acid[10] (**5**; 0.649 g, 2 mmol) in dry pyridine (5 cm³) was added dichloramine-T ($TsNCl_2$; 0.240 g, 1 mmol) at room temperature. After a few minutes the product **2** began to crystallize. The mixture was allowed to stand for 1 h, then the crystals formed were isolated (0.420 g, 65%), m.p. 238–243 °C. On the basis of its IR spectrum the product was identical with that obtained by path ii.

(ii) To a solution of 2-(8-carboxy-1-naphthylsulfinyl)benzoic acid monohydrate[10] (**7**; 177.0 g, 0.495 mol) in dry pyridine (1150 cm³) was added acetic anhydride (105 cm³) at 100 °C (steam bath) for 3 h. On cooling to room temperature, the spirosulfurane **2** separated as white, bright crystals which were isolated (141.4 g, 89%), m.p. 248–253 °C (Found: C, 66.85; H, 3.4; O, 20.3; S, 9.9. $C_{18}H_{10}O_4S$ requires: C, 67.07; H, 3.13; O, 19.86; S, 9.95%); ν_{max}(KBr)/cm^{-1} 1712vs, 1675vs (C=O), 1270s, 1240s, 1125s (Ar–CO–O) and 796s, 749s (O–S–O).

3H-2,1-*Benzoxathiole*-1-*spiro*-1′-(3H-*dibenzo*[c,e]-2,1-*oxathiepine*)-3,3′-*dione* (**3**). (i) The mixture of crude ethyl 2-iodobiphenyl-2′-carboxylate[9] (**9**; 44.6 g, b.p. 150–200 °C/3 Torr), thiosalicylic acid (**10**; 14.0 g, 0.09 mol), Cu_2O (6.0 g, 0.042 mol) and dry pyridine (180 cm³) was refluxed for 3 h under N_2. After cooling to room temperature the mixture was added to aqueous conc. HCl (300 cm³), then the gummy product washed with water by decantation. The residue was dissolved in aqueous NaOH (90 g of NaOH in 1000 cm³ of water), boiled for 2 h and filtered. The filtrate was acidified with conc. HCl, the precipitate filtered and dried (34 g) then boiled in acetonitrile (100 cm³). On cooling the crude 2-(1′-carboxy-1-biphenylylthio)benzoic acid (**11**) separated (16.3 g) and was purified by recrystallization from AcOH (60 cm³) to get the pure product **11** with 0.5 AcOH (13.4 g, 39%), m.p. 225–235 °C (Found: C, 65.4; H, 4.55; O, 21.45; S, 7.95. $C_{20}H_{14}O_4S{\cdot}0.5CH_3CO_2H$ requires: C, 66.30; H, 4.23; O, 21.03; S, 8.43%); ν_{max}(KBr)/cm^{-1} 3200–2400br (OH), and 1687vs (C=O).

(ii) The sulfide **11** (**11**·0.5AcOH; 3.64 g, 9.6 mmol) was dissolved in hot, dry AcOH (25 cm³) and iodobenzene diacetate [PhI(OAc)$_2$; 3.22 g, 10 mmol] was added at 30–40 °C. Next day the crystals of the spirosulfurane **3** were isolated (1.34 g, 40%),

Table 4 X-ray crystallographic data for spirosulfuranes **1**–**4**

	Spirosulfuranes			
	1	**2**	**3**	**4**
Formula	$C_{14}H_8O_4S$	$C_{18}H_{10}O_4S$	$C_{20}H_{12}O_4S$	$C_{22}H_{12}O_4S$
Mol. wt.	272.28	322.34	348.38	372.40
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Orthorhombic
Space group	*Fdd*2	$P\bar{1}$	*Pbca*	*Fdd*2
a/Å	20.092(5)	7.440(1)	8.317(1)	25.026(3)
b/Å	27.765(3)	8.765(1)	16.308(1)	26.182(3)
c/Å	4.228(1)	11.144(1)	23.439(1)	4.883(1)
α/°	90	85.86(1)	90	90
β/°	90	78.80(1)	90	90
γ/°	90	75.64(1)	90	90
Cell volume/Å^3	2358.6(18)	690.3(2)	3179.2(7)	3199.6(14)
Z	8	2	8	8
F(000)	1120	332	1440	1536
D_{calc}/g cm^{-3}	1.533	1.550	1.460	1.550
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan rate deg/min in	1–10	1–20	1–20	1–20
Scan width	0.65 + 0.30 tanθ	0.40 + 14 tanθ	0.60 + 14 tanθ	0.45 + 14 tanθ
Intensity variation	none	none	none	none
X-radiation	Mo-Kα	Cu-Kα	Cu-Kα	Cu-Kα
λ/Å	0.71069	1.54184	1.54184	1.54184
μ/cm^{-1}	2.29	22.1	19.6	19.9
Crystal size (mm)	0.1 × 0.12 × 0.50	0.25 × 0.28 × 0.30	0.17 × 0.28 × 0.35	0.25 × 0.22 × 0.35
Max. transmiss. coef.	—	1.28	1.15	1.45
Min. transmiss. coef.	—	0.79	0.83	0.86
θ range deg.	1.5–25	1.5–75	3–150	1.5–75
h range	−23/23	0/9	0/10	0/31
k range	−32/32	−10/10	0/20	0/32
l range	0/4	−13/13	0/29	0/6
Total reflections	2055	4675	3283	1022
Non zero reflections	583 (merged)	2745	2937	935
Number of reflections used in refinement	555	2573	2546	888
σ level	2.0	3.0	3.0	3.0
weighting scheme	$1/\sigma^2(F_0) + kF_0^2$ $k = 0.01885$	$4F_0^2/\sigma^2(F_0)^2$	$4F_0^2/\sigma^2(F_0)^2$	$4F_0^2/\sigma^2(F_0)^2$
$R = \Sigma\Delta F/\Sigma F_0$	0.087	0.042	0.056	0.034
$R = \Sigma w(\Delta F^2)/\Sigma\lvert F_0{}^2\rvert$	0.081	0.075	0.070	0.087
$S = \Sigma(w\lvert F_o\rvert - \lvert F_c\rvert^2/(N_o\text{-}P)^{\frac{1}{2}}$	2.30	3.31	2.32	3.98
Max. LS shift to error ratio	0.8	0.035	0.71	0.35
Max. e Å^{-3}	1.17(9)	0.27(5)	0.38(8)	0.06(2)

m.p. 150–190 °C (decomp.) (Found: C, 67.6; H, 3.4; S, 9.1. $C_{20}H_{12}O_4S$ requires: C, 68.95; H, 3.47; S, 9.20%); ν_{max}(KBr)/cm^{-1} 1724vs, 1680vs (C=O), 1242s, 1118s (Ar–CO–O) and 822s, 759s (O–S–O); *m*/*z* 348 (M$^+$, 10%) and 349 (MH$^+$, 73%).

2-(1′-*Carboxy*-1-*biphenylylsulfinyl*)*benzoic acid* (**12**). (iii) To a solution of sulfide **11** (**11**·0.5AcOH; 12.8 g, 0.034 mol) in pyridine (68 cm^3) was added water (10 cm^3) then PTAB[10] [$(PhN^+(CH_3)_3Br^-\cdot Br_2$; 12.7 g, 0.034 mol] at room temperature and the mixture was stirred for 1 h. The mixture was poured into 10% aqueous H_2SO_4 (950 cm^3) and the crystals separated were filtered and dried to give the crude sulfoxide **12** (8.9 g, 72%), which was recrystallized from boiling water (9 cm^3) and AcOH (45 cm^3) to yield the pure product **12** (4.90 g, 39%), m.p. 130–140 °C (Found: S, 8.4. $C_{20}H_{14}O_5S$ requires: S, 8.75%); ν_{max}(KBr)/cm^{-1} 3200–2300br (OH), 1685vs (C=O) and 968s (S=O).

The reaction of the sulfoxide-dicarboxylic acid **12** *with acetic anhydride in pyridine*. (iv) To a solution of the sulfoxide **12** (0.54 g, 1.47 mmol) in dry pyridine (3 cm^3) was added Ac_2O (1.5 cm^3) at 100 °C and then the mixture was allowed to cool to room temperature. On addition of dry diethyl ether (2 cm^3) crystals were separated and isolated next day (0.39 g, 76%). The IR spectrum of the product showed a mixture of the spirosulfurane **3** (30–40%) and cyclic acid anhydride **13** (60–70%).

2-(1′-*Carboxy*-1-*biphenylylsulfinyl*)*benzoic anhydride* (**13**). (v) The solution of spirosulfurane **3** (1 g, 2.9 mmol) in dry pyridine (10 cm^3) was heated on a steam bath (100 °C) for 30 min, and cooled to room temperature, before addition of dry diethyl ether. Next day the crystals of cyclic anhydride **13** were isolated (0.73 g, 73%) m.p. 173–180 °C (Found C, 67.6; H, 3.5; S, 9.1. $C_{20}H_{12}O_4S$ requires: C, 68.95; H, 3.47; S, 9.20%); ν_{max}(KBr)/cm^{-1} 1805vs, 1730m (CO–O–CO) and 1018vs (S=O).

(vi) The sulfoxide **12** (1.0 g, 2.7 mmol) was dissolved in a mixture of AcOH (9 cm^3) and Ac_2O (1 cm^3) and refluxed for 5 min. After cooling, the cyclic anhydride **13** was precipitated with dry diethyl ether and isolated (0.68 g, 72%). The product was identical with that one obtained by path v.

(vii) The sulfoxide **12** (2.18 g, 5.9 mmol) was dissolved in the mixture of DMF (3 cm^3), Et_3N (1.64 cm^3, 11.8 mmol) and AcCl (0.43 cm^3, 6 mmol) was added dropwise with cold water cooling. The mixture was stirred for 5 min, then poured into ice-water (25 cm^3) and the solid product **13** isolated (0.6 g, 29%), which was identical with that one obtained by path v.

1,1′-*Spirobi*-(3H-*naphtho*[1,8-d,e]-2,1-*oxathiine*)-3,3′-*dione* (**4**). (i) To a solution of bis(8-carboxy-1-naphthyl) sulfide[20] (**6**, 0.75 g, 2.0 mmol) in dry pyridine (5 cm^3) was added $TsNCl_2$ (0.24 g, 1 mmol) at room temperature. Next day the white crystals of the spirosulfurane **4** were isolated from the reaction mixture (0.53 g, 71%), m.p. *ca.* 230 °C. According to its IR spectrum, the product obtained in this way was practically identical with the spirosulfurane **4** but it was contaminated with some unidentified materials. It could be purified by hydrolysis into the corresponding sulfoxide **8** and subsequent transformation into the spirosulfurane **4** by method ii. Hydrolysis: The suspension of the product **4** (0.52 g, 14 mmol) obtained by method i in water (15 cm^3) was boiled (100 °C) for 10 h, and after cooling to room temperature the solid sulfoxide **8** isolated (0.53 g, 96%), m.p. 223–225 °C (lit.[10] m.p. 223–225 °C). (ii) To a solution of bis(8-carboxy-1-naphthyl) sulfoxide monohydrate[10] (**8**; 4.5 g, 11 mmol) in dry pyridine (50 cm^3) was added Ac_2O (5 cm^3) at 100 °C for 3 h. On cooling to room temperature the crystals of the spirosulfurane **4** separated and were isolated (3.1 g, 76%), m.p. 237–239 °C (decomp.) (Found: C, 70.75; H, 3.35; O, 17.5; S, 8.5. $C_{22}H_{12}O_4S$ requires: C, 70.95; H, 3.35; O, 17.19; S, 8.61%); ν_{max}(KBr)/cm^{-1} 1683vs (C=O), 1260s, 1140s (Ar–CO–O) and 786s, 764s (O–S–O).

Structure Analysis and Refinements.—X-ray quality single crystals were grown from the Ac_2O/pyridine reaction mixtures for the spirosulfuranes **1**, **2** and **4** and from dichloromethane–pentane solvent mixture for the spirosulfurane **3**. Table 4 summarizes the relevant data concerning the crystal structure analyses. Each data set was collected at room temperature (296 ± 1 K) 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 Lorentz and polarization effects. In the course of the refinement each data set (except for **1**) was corrected for absorption by the use of program DIFABS.[21]

Structures of the spirosulfuranes **2** and **4** were solved by the heavy atom method and subsequent Fourier syntheses, while that of the spirosulfurane **3** was inferred from direct methods using the MULTAN82 program.[22] The structure of the spirosulfurane **1** had been determined earlier.[4] After an $F2dd \longrightarrow Fdd2$ transformation of the lattice parameters the known atomic coordinates of **1** were refined on the new data set. Although the new data set provided much better refinement than before, the low scattering power of the tiny crystals of **1** (the larger and longer fibrous needles were of very poor quality) against Mo-Kα radiation permitted us to increase l_{max} only from 3 to 4. This, of course hindered the refinement; for the quasi-isostructural **4** ($l_{max} = 6$) the refinement resulted in considerably better atomic parameters. The atomic positions for each structure were refined by least squares in anisotropic mode. The hydrogen positions were generated from assumed geometries and treated in different ways as follows: They were refined isotropically only for **2**, whereas in case of **3** and **4** they were only included in the final structure factor calculations with a mean isotropic temperature factor ($B_{iH} = B_{ic} + 1$ Å^2). Owing to the unfavourable limit of the l index, the four symmetry-independent H atoms of **1** were introduced to SF calculation with one common isotropic temperature factor ($B = 5.9$ Å^2). All calculations employed the Enraf-Nonius Structure Determination Package.[23] Scattering factors including corrections for anomalous scattering were taken from the same package.

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

Acknowledgements

The authors thank Dr. Kálmán Ujszászy for the mass spectra analyses. This work was supported by the Hungarian Scientific Research Foundation (OTKA, No. 2238).

References

1 Part 2, I. Kapovits, J. Rábai, F. Ruff, A. Kucsman and B. Tanács, *Tetrahedron*, 1979, **35**, 1875.

2 E. Vass, F. Ruff, I. Kapovits, J. Rábai and D. Szabó, *J. Chem. Soc., Perkin Trans. 2*, 1993, following paper.

3 I. Kapovits and A. Kálmán, *J. Chem. Soc., Chem. Commun.*, 1971, 649.

4 A. Kálmán, K. Sasvári and I. Kapovits, *Acta Crystallogr., Sect. B*, 1973, **29**, 355.

5 I. Kapovits, J. Rábai, F. Ruff and Á. Kucsman, *Tetrahedron*, 1979, **35**, 1869.

6 For review see: R. A. Hayes and J. C. Martin, in *Studies in Organic Chemistry 19, Organic Sulfur Chemistry*, eds. F. Bernardi, I. G. Csizmadia and A. Mangini, Elsevier, Amsterdam, 1985, Chap. 8, p. 408.

7 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960, 3rd edn., p. 221.

8 J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 54; V. B. Koutecky and J. I. Musher, *Theor. Chim. Acta* (*Berl.*) 1974, **33**, 227.

9 H. A. Staab, E. Wehinger and W. Thorwart, *Chem. Ber.*, 1972, **105**, 2290.

10 J. Rábai, I. Kapovits, B. Tanács and J. Tamás, *Synthesis*, 1990, 847.

11 A. Kálmán, L. Párkányi and D. Szabó, *J. Mol. Struct.*, submitted for publication.

12 F. H. Allen, O. Kennard, D. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

13 W. Y. Lam, E. N. Duesler and J. C. Martin, *J. Org. Chem.*, 1981, **103**, 127.

14 R. Bucourt, *Top Stereochem.*, 1974, **8**, 159.

15 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.

16 J. B. Hendrickson, *J. Am. Chem. Soc.*, 1967, **89**, 7036.

17 A. Kálmán, L. Párkányi and Gy. Argay, *Acta Crystallogr. Sect. B*, submitted for publication.

18 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press: Ithaca, New York, 1960, 3rd edn., p. 260.

19 M. Bihari, J. Tamás, I. Kapovits and J. Rábai, *Acta Chim. Acad. Sci. Hung.*, 1984, **115**, 39.

20 J. Rábai, *Synthesis*, 1989, 523.

21 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, 1983, **39**, 158.

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 Enraf-Nonius, SDP-Plus Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1983.

Paper 3/00490B
Received *26th January* 1993
Accepted *5th February* 1993

---

* For details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.