

Stereospecific synthesis and absolute configuration of optically active diaryl(acyloxy)(alkoxy)spiro- λ^4 -sulfanes

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Abstract: Optically active (*R*)-(+)-1,1'-spirobi[3*H*-2,1-benzoxathiol]-3-one (*R*)-(+)-**5**, the (*R*)-(+ and (*S*)-(-) enantiomers of spiro[3*H*-2,1-benzoxathiol-1,1'-naphtho[1,8-*d,e*]-3*H*-2,1-oxathiin-3-one] (*R*)-(+)-**8** and (*S*)-(-)-**8**, and (*S*)-(+)-spiro[3*H*-2,1-benzoxathiol-3-one-1,1'-naphtho[1,8-*d,e*]-3*H*-2,1-oxathiine] (*S*)-(+)-**10** all belonging to the class of diaryl(acyloxy)-(alkoxy)spiro- λ^4 -sulfanes (spirosulfuranes) were prepared by dehydration of the optically active diaryl sulfoxides (*R*)-(+)-**4**, (*R*)-(-)-**7**, (*S*)-(+)-**7**, and (*S*)-(+)-**9**, respectively, all of them carrying reactive CH₂OH and COOH substituents. (*R*)-(+)-5*H*,7*H*-dibenzo[*c,f*]-1,5-oxathiocin-5-one 12-oxide (*R*)-(+)-**6**, a sulfoxide-lactone isomer of spiro- λ^4 -sulfane (*R*)-(+)-**5** was also obtained from (*R*)-(+)-**4** by dehydration. The molecular structures including the absolute configurations were determined for (*R*)-(+)-**5**, (*R*)-(+)-**6** and (*R*)-(+)-**8** by X-ray diffraction method. Relevant bond length and angle data are listed. Sulfur configurations, solid-state conformations and a stereospecific pathway for the dehydration of sulfoxides are discussed in detail. © 1997 Elsevier Science Ltd

Introduction

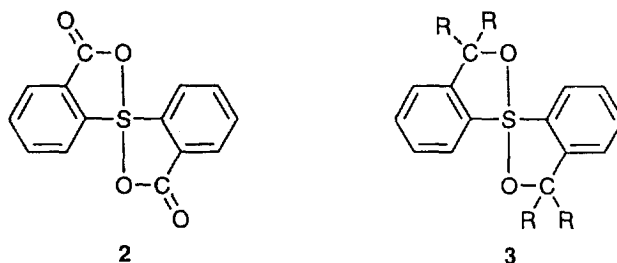
Spiro- λ^4 -sulfanes (earlier spirosulfuranes), the stable organic analogues of the simple SF₄ molecule are excellent models for studying both the hypervalent bonding systems about the four-coordinated sulfur(IV) atom and reactions occurring at sulfur exhibiting trigonal-bipyramidal configuration. Diaryl-spiro- λ^4 -sulfanes with apical ligands of O-acyl,¹⁻³ O-alkyl,⁴⁻⁶ or N-acyl⁷⁻¹⁰ type can be well prepared from diaryl sulfides having two reactive groups (e.g. COOH, CH₂OH, NHAc, NHR) by oxidation (starting with S-halogenation)¹¹ or from the corresponding diaryl sulfoxides by dehydration.¹²

Owing to the two spiro-rings with central sulfur atom spiro- λ^4 -sulfanes are chiral even if they are of (a,b)S(a,b) type exhibiting C₂-symmetry as shown schematically by the enantiomeric structures **1A** and **1B**.

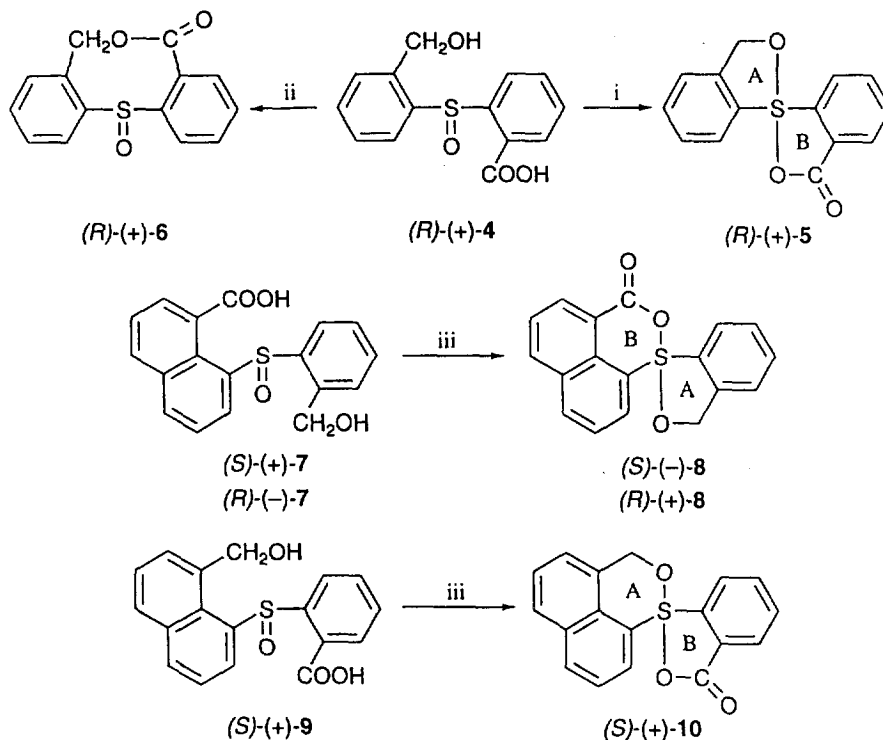


Thus compound **2**, the first known spiro- λ^4 -sulfane,^{1,2} as well as its analogue with two naphthalene rings³ could be separated into enantiomers by a chromatographic method.^{13,14} By using a kinetic resolution procedure some racemic spiro- λ^4 -sulfanes of (a,b)S(a,b) type, e.g. **3** (R=Me,⁵ or CF₃ with *t*-Bu substituents in *para* positions⁴) were also separated into enantiomers.¹⁵ In another approach prochiral sulfoxide diols were dehydrated under asymmetric conditions to yield spiro- λ^4 -sulfanes (e.g. **3**) with a rather low enantiomeric excess (below 5%).¹⁶

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The first attempt in 1978 to obtain optically active spiro- λ^4 -sulfanes followed another way.¹⁷ We prepared the diphenyl sulfoxide **4** carrying *o*-CH₂OH and *o'*-COOH substituents (see Scheme 1) and resolved it into enantiomers. By using acetyl chloride as dehydrating agent both of them were submitted to dehydration at low temperature (-70°C) in the presence of two eq triethylamine. Unfortunately the dehydrated products which retained optical activity were wrongly assigned as the enantiomers of spiro- λ^4 -sulfane **5**, however the enantiomers of the isomeric sulfoxide-lactone **6** were formed in the above case.^{5,18}



Scheme 1. Conversion of CH₂OH- and COOH-disubstituted diaryl sulfoxides into spiro- λ^4 -sulfanes and a sulfoxide-lactone. *Reagents and conditions:* (i) AcCl, 1 eq Et₃N, DMF, -60°C , then 1,2-dichloroethane, 83°C , 20 min; (ii) AcCl, 2 eq Et₃N, DMF, -60°C ; (iii) DCC, CH₂Cl₂, 20°C , 4 h.

Having revised the experimental conditions, we report now the first stereospecific synthesis of an optically active spiro- λ^4 -sulfane of (ab)S(a'b) type, $(R)\text{-}(+)\text{-5}$, as well as that of the isomeric sulfoxide-lactone $(R)\text{-}(+)\text{-6}$, starting from the sulfoxide $(R)\text{-}(+)\text{-4}$ ¹⁹ obtained earlier in pure form (cf. Scheme 1). In a similar way, the sulfoxides $(R)\text{-}(-)\text{-7}$,¹⁹ $(S)\text{-}(+)\text{-7}$,¹⁹ and $(S)\text{-}(+)\text{-9}$ ¹⁹ were also dehydrated to the corresponding spiro- λ^4 -sulfanes $(R)\text{-}(+)\text{-8}$, $(S)\text{-}(-)\text{-8}$, and $(S)\text{-}(+)\text{-10}$, respectively (cf. Scheme 1).

The molecular structures including absolute configurations for $(R)\text{-}(+)\text{-5}$, $(R)\text{-}(+)\text{-6}$, and $(R)\text{-}(+)\text{-8}$

were determined by X-ray diffraction method, whereas the tentative assignment of (*S*)-(+)-**10** was based on the comparative analysis of CD-spectra that will be explained in detail elsewhere.²⁰ In designating the configuration of the central sulfur atom in spiro- λ^4 -sulfanes the convention proposed by Martin and Balthazor²¹ was used.

Results and discussion

Synthesis (see Scheme 1)

(*R*)-(+)-2-[(2-Hydroxymethylphenyl)sulfinyl]benzoic acid¹⁹ {sulfoxide (*R*)-(+)-**4**} was treated at -60°C with acetyl chloride in a DMF solution containing one eq triethylamine, then the reaction product dissolved in 1,2-dichloroethane was boiled for 20 min to give (*R*)-(+)-1,1'-spirobi[3*H*-2,1-benzoxathiol]-3-one {spiro- λ^4 -sulfane (*R*)-(+)-**5**}. When the above reaction was carried out in the presence of two eq triethylamine, the product was (*R*)-(+)-5*H*,7*H*-dibenzo[*c,f*]-1,5-oxathiocin-5-one 12-oxide {sulfoxide-lactone (*R*)-(+)-**6**}.

(*R*)-(-)- and (*S*)-(+)-8-[(2-Hydroxymethylphenyl)sulfinyl]-1-naphthoic acids¹⁹ {sulfoxides (*R*)-(-)-**7** and (*S*)-(+)-**7**} were dehydrated to (*R*)-(-)- and (*S*)-(-)-spiro[3*H*-2,1-benzoxathiol-1,1'-naphtho[1,8-*d,e*]-3*H*-2,1-oxathiin-3-one] {spiro- λ^4 -sulfanes (*R*)-(+)-**8** and (*S*)-(-)-**8**}, respectively, by a slight modification of the DCC method used for the synthesis of racemic **8**.⁶ The crystals of (*R*)-(+)-**8** was used for an X-ray study.

The synthesis of optically active (*S*)-(+)-spiro[3*H*-2,1-benzoxathiol-3-one-1,1'-naphtho[1,8-*d,e*]-3*H*-2,1-oxathiine] {spiro- λ^4 -sulfane (*S*)-(+)-**10**} followed another way than the synthesis of racemic **10** described in Ref.⁶ In the present case (*S*)-(+)-2-[(8-hydroxymethyl-1-naphthyl)sulfinyl]benzoic acid¹⁹ {sulfoxide (*S*)-(+)-**9**} was treated with DCC in dichloromethane at 20°C . From the product obtained, however, we could not grow X-ray quality crystals, so the absolute configuration of (+)-**10** could not be determined by X-ray diffraction method. On the basis of analogy and that of a comparative analysis of CD spectra,²⁰ however, (+)-**10** may be tentatively assigned as (*S*)-(+)-**10**. The CD spectra of spiro- λ^4 -sulfanes (*R*)-(+)-**5**, (*R*)-(+)-**8**, (*S*)-(+)-**10** and that of the sulfoxide-lactone (*R*)-(+)-**6** are shown in Figure 1.

Enantiomeric excess

The enantiomeric excess of **5** was determined by HPLC method,²² whereas **8** and **10** were hydrolysed into the starting sulfoxides (**7** and **9**) and the optical activity measured.²³ The following minimal enantiomeric excess data were obtained: >99.5% for (+)-**5**, >90% for (-)-**8**, and (+)-**10**.

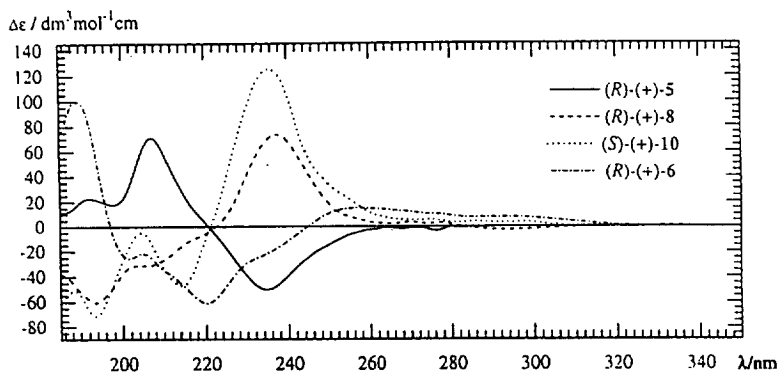


Figure 1. CD spectra of spiro- λ^4 -sulfanes (*R*)-(+)-**5**, (*R*)-(+)-**8**, (*S*)-(+)-**10** and that of sulfoxide-lactone (*R*)-(+)-**6**.

Molecular structure and absolute configuration

The molecular structures of compounds (*R*)-(+)-**5**, (*R*)-(+)-**6** and (*R*)-(+)-**8** as determined by single-crystal X-ray diffraction method are shown in Figs 2–4 together with selected interatomic distances and angles.

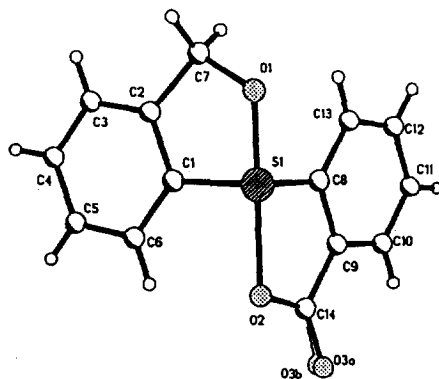


Figure 2. Perspective representation of (*R*)-(+)-**5** spiro- λ^4 -sulfane molecule. Selected bond lengths (Å) and angles (deg) are as follows: S(1)–O(1) 1.707(3), S(1)–O(2) 2.052(4), S(1)–C(1) 1.795(5), S(1)–C(8) 1.799(5), C(7)–O(1) 1.435(7), C(14)–O(2) 1.315(7), C(14)–O(3A) 1.23(1). ϑ_1 (O1–S1–O2) 179.7(3), ϑ_2 (C1–S1–C8) 105.5(4), ϑ_3 (C1–S1–O2) 89.9(3), ϑ_4 (C8–S1–O1) 96.5(3), ϑ_5 (C1–S1–O1) 89.8(3), ϑ_6 (S1–O1–C7) 116.7(3), ϑ_7 (O1–C7–C2) 106.3(7), ϑ_8 (C7–C2–C1) 113.7(7), ϑ_9 (C2–C1–S1) 112.0(6), ϑ_{10} (C8–S1–O2) 83.7(3), ϑ_{11} (S1–O2–C14) 112.8(6), ϑ_{12} (O2–C14–C9) 112.5(9), ϑ_{13} (C14–C9–C8) 114.5(8), ϑ_{14} (C9–C8–S1) 116.4(6). φ_1 (O1–S1–C1–C2) 5.2(5), φ_2 (S1–C1–C2–C7) 1.4(5), φ_3 (C1–C2–C7–O1) –8.8(7), φ_4 (C2–C7–O1–S1) 13.2(4), φ_5 (C7–O1–S1–C1) –11.1(6), φ_6 (O2–S1–C8–C9) –2.1(5), φ_7 (S1–C8–C9–C14) 0.4(6), φ_8 (C8–C9–C14–O2) 2.8(8), φ_9 (C9–C14–O2–S1) –4.3(4), φ_{10} (C14–O2–S1–C8) 3.8(7), φ_{11} (S1–O2–C14–O3A) 166.7(2), φ_{12} (C8–C9–C14–O3A) –168.2(1), φ_{13} (O2–S1–C1–C2) –174.9(8), φ_{14} (O1–S1–C8–C9) 178.1(8), φ_{15} (C8–S1–C1–C2) –91.5(5), φ_{16} (C1–S1–C8–C9) –90.2(7).

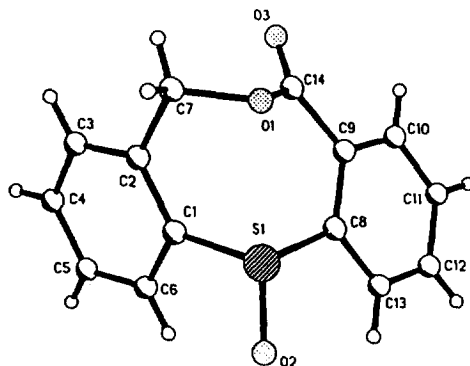


Figure 3. Perspective representation of sulfoxide-lactone (*R*)-(+)-**6** molecule. Selected bond lengths (Å) and angles (deg) are as follows: S(1)···O(1) 2.602(1), S(1)–O(2) 1.487(2), S(1)–C(1) 1.826(2), S(1)–C(8) 1.829(2), C(14)–O(3) 1.194(2), C(14)–O(1) 1.360(2), C(7)–O(1) 1.458(2). ϑ_1 (O2–S1···O1) 177.4(1), ϑ_2 (C1–S1–C8) 98.0(1), ϑ_3 (C1–S1–O2) 105.3(2), ϑ_4 (C8–S1–O2) 104.1(2), ϑ_5 (C1–S1···O1) 73.9(1), ϑ_6 (C8–S1···O1) 73.6(1), ϑ_7 (O1–C14–O3) 123.9(3), ϑ_8 (C9–C14–O1) 109.9(3), ϑ_9 (C9–C14–O3) 126.1(3), ϑ_4 (C7–O1–C14) 115.2(2). φ_1 (O1–C7–C2–C1) 32.1(3), φ_2 (C7–C2–C1–S1) 6.2(2), φ_3 (C2–C1–S1–C8) –93.4(2), φ_4 (C2–C1–S1–O2) 159.5(3), φ_5 (C1–S1–C8–C9) 62.3(3), φ_6 (O2–S1–C8–C9) 170.4(3), φ_7 (S1–C8–C9–C14) –6.3(2), φ_8 (C8–C9–C14–O1) 28.4(3), φ_9 (C8–C9–C14–O3) –149.9(3), φ_{10} (C9–C14–O1–C7) –133.8(3), φ_{11} (O3–C14–O1–C7) 44.5(3), φ_{12} (C14–O1–C7–C2) 69.0(3).

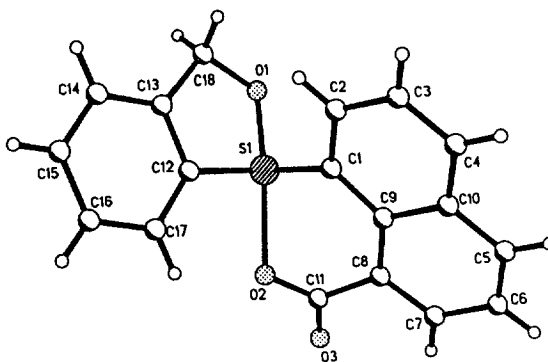


Figure 4. Perspective representation of spiro- λ^4 -sulfane (*R*)-(+)-**8** molecule. Selected bond lengths (Å) and angles (deg) are as follows: S(1)–O(1) 1.661(1), S(1)–O(2) 2.129(2), S(1)–C(1) 1.806(2), S(1)–C(12) 1.791(1), C(18)–O(1) 1.440(2), C(11)–O(2) 1.286(2), C(11)–O(3) 1.233(2). ϑ_1 (O1–S1–O2) 172.7(1), ϑ_2 (C1–S1–C12) 104.1(1), ϑ_3 (C1–S1–O1) 99.5(1), ϑ_4 (C12–S1–O2) 87.4(1), ϑ_5 (C12–S1–O1) 91.5(1), ϑ_6 (S1–O1–C18) 117.2(2), ϑ_7 (O1–C18–C13) 106.4(3), ϑ_8 (C18–C13–C12) 114.4(3), ϑ_9 (C13–C12–S1) 110.5(2), ϑ_{10} (C1–S1–O2) 87.7(1), ϑ_{11} (S1–O2–C11) 113.0(2), ϑ_{12} (O2–C11–C8) 115.5(2), ϑ_{13} (C11–C8–C9) 121.9 (2), ϑ_{14} (C8–C9–C1) 125.6(3), ϑ_{15} (C9–C1–S1) 120.3(2). φ_1 (O1–S1–C12–C13) –2.6(2), φ_2 (S1–C12–C13–C18) 1.6(2), φ_3 (C12–C13–C18–O1) 0.6(2), φ_4 (C13–C18–O1–S1) –2.7(2), φ_5 (C18–O1–S1–C12) 3.2(2), φ_6 (O2–S1–C1–C9) 40.1(2), φ_7 (S1–C1–C9–C8) –13.1(2), φ_8 (C1–C9–C8–C11) –13.2(3), φ_9 (C9–C8–C11–O2) –14.1(3), φ_{10} (C8–C11–O2–S1) 55.4(2), φ_{11} (C11–O2–S1–C1) –65.3(2), φ_{12} (S1–O2–C11–O3) –128.4(4), φ_{13} (C9–C8–C11–O3) 169.5(3), φ_{14} (O2–S1–C12–C13) –175.4(3), φ_{15} (O1–S1–C1–C9) –139.2(3), φ_{16} (C1–S1–C12–C13) 97.6(2), φ_{17} (C12–S1–C1–C9) 126.8(2).

Sulfur configuration

Figures 2–4 show that the configuration of the stereogenic sulfur atom in compounds (*R*)-(+)-**5**, (*R*)-(+)-**6** and (*R*)-(+)-**8** is the same as in the precursor sulfoxides (*R*)-(+)-**4** and (*R*)-(–)-**7**. The trigonal-bipyramidal geometry in spiro- λ^4 -sulfanes (*R*)-(+)-**5** and (*R*)-(+)-**8** is reflected by the almost linear arrangement of the axial O1–S–O2 moiety ($\vartheta_1=180^\circ$ and 173° , respectively) and, as is expected, the axial S–O bonds are perpendicular to the C(ar)–S–C(ar) plane ($\vartheta_5=90^\circ$ and 91° , respectively). Owing to the cyclic structure of sulfoxide-lactone (*R*)-(+)-**6** there exists an intramolecular S \cdots O close contact between the ring hetero atoms. As in other cases (cf. Ref.²⁴) the O2–S \cdots O1 sequence is almost linear ($\vartheta_1=177^\circ$), and the S \cdots O1 distance (2.60 Å) is markedly shorter than the sum of the van der Waals radii (3.25 Å²⁵).

Bond lengths and angles

Like other spiro- λ^4 -sulfanes of diaryl(acyloxy)(alkoxy) type⁶ the S–O(alkoxy) and S–O(acyloxy) bonds differ markedly in both (*R*)-(+)-**5** and (*R*)-(+)-**8**. The former bond lengths (1.71 Å in **5** and 1.66 Å in **8**) correspond to a usual covalent single bond (cf. the value of 1.70 Å²⁵ given for the sum of the covalent radii), whereas the latter bond lengths (2.05 Å in **5** and 2.13 Å in **8**) point to an elongated and markedly polarized hypervalent bond that is not far from a sulfonium–carboxylate zwitterion. The axial O(alkoxy)–S–O(acyloxy) distances (3.76 Å in **5** and 3.79 Å in **8**), which are characteristic of the different type of spiro- λ^4 -sulfanes, fall in the region C (3.73–3.81 Å) given in Ref.⁶ for diaryl(acyloxy)-(alkoxy)spiro- λ^4 -sulfanes. Other bond lengths and angles also correspond to those obtained earlier⁶ for spiro- λ^4 -sulfanes of this type. It may be mentioned that there are no marked differences in geometry data of optically active (*R*)-(+)-**8** and those of racemic **8** published in Ref.⁶.

Data obtained for the sulfoxide-lactone (*R*)-(+)-**6** are remarkably like those of precursor sulfoxide (*R*)-(+)-**4**. The C=O bond length (1.19 Å) and ν (C=O) frequency (1739 cm^{–1}) are in accordance with the lactone structure of (*R*)-(+)-**6**. On the other hand, the significant elongation of the C=O bond length (1.23 Å) and the strikingly low ν (C=O) frequency (1655 cm^{–1}) observed for the isomeric spiro- λ^4 -

sulfane (*R*)-(+)-**5** may be explained by an electronic structure shifted toward a sulfonium–carboxylate zwitterion.

Conformation

Torsion angles show that the conformation of the five-membered spirorings in spiro- λ^4 -sulfanes (*R*)-(+)-**5** and (*R*)-(+)-**8** vary from an almost planar [$\varphi_{\max}=4^\circ$ and 3° for **5** (ring B) and **8** (ring A), respectively] to a twisted envelope shape [$\varphi_{\min}=1^\circ$ and $\varphi_{\max}=13^\circ$ for **5** (ring A)]. The six-membered spiroring B in **8** assume an inverted half-chair shape that may be classified as a 1,3-diplanar form ($\varphi_{\min}=-13^\circ$ and -14° , $\varphi_{\max}=-65^\circ$), as in the case of the racemic form of **8** (cf. Ref.⁶).

The molecular shape of (*R*)-(+)-**5**, (*R*)-(+)-**6** and (*R*)-(+)-**8** can be characterized by the two angles between the C(ar)–S–C(ar) moiety and the planes of the aromatic rings A' and B'. The corresponding C(ar)–S–C(ar)–C(ar) dihedral angles $\varphi_{A'}=-91^\circ$, -93° , and 98° for rings A', and $\varphi_{B'}=-90^\circ$, 62° , and 127° for rings B' in **5**, **6**, and **8**, respectively, point to a butterfly conformation in **5**, and an axial-twist conformation in **6** and **8** (cf. Ref.¹⁹). In spiro- λ^4 -sulfanes (*R*)-(+)-**5** and (*R*)-(+)-**8** the acyloxy group is nearly coplanar with ring B', as indicated by the torsion angles C(ar)–C(ar)–C(sp²)–O= -168° , and 169° , respectively, whereas the corresponding torsion angle in the sulfoxide-lactone (*R*)-(+)-**6** is only -150° .

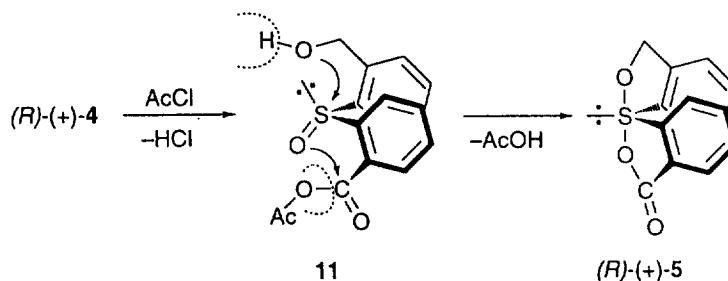
Stereomechanism

Molecular structure determinations clearly show that the conversion of optically active sulfoxides (*R*)-(+)-**4** and (*R*)-(–)-**7** into spiro- λ^4 -sulfanes (*R*)-(+)-**5** and (*R*)-(+)-**8**, respectively, proceeds with “retention of configuration”. In the given cases this means that the C_{ar}(acyl-O)→C_{ar}(alkyl-O)→lone pair sequence of substituents attached to the chiral sulfur atom traces the same direction in both cases if the structure is viewed from the side of the sulfinyl-oxygen in sulfoxide (Cahn–Ingold–Prelog convention) or from the side of the acyloxy-oxygen in spiro- λ^4 -sulfane (Martin–Balthazor convention²¹). The designation is (*R*) for both sulfoxides (+)-**4** and (–)-**7**, and spiro- λ^4 -sulfanes (+)-**5** and (+)-**8** because the order of decreasing priority represents a clockwise sequence.

If we consider the dehydration of hydroxymethyl-carboxy-disubstituted diaryl sulfoxides with acetyl chloride, four simple spiro- λ^4 -sulfane-forming mechanisms may be taken into account: the sulfinyl-oxygen attacks the carbon atom of the acetylated carboxy group (pathway a) or that of the acetylated hydroxymethyl group (pathway b); the sulfur atom of the acetylated sulfinyl group is attacked by carboxy-oxygen (pathway c) or by hydroxymethyl-oxygen (pathway d). (The reaction of the carboxy and hydroxymethyl groups involving an activated species leads obviously to the formation of an eight-membered sulfoxide-lactone without any change in the sulfinyl moiety.) The retention of configuration may occur only in cases (a) and (d) from which pathway (a) shown in Scheme 2 can be supported by the following facts. (i) A high degree ($\approx 70\%$) of ¹⁸O-retention was observed earlier in the conversion of ¹⁸O-labelled sulfoxides into spiro- λ^4 -sulfanes when the reaction was performed at low temperature by acetyl chloride in the presence of triethylamine.¹² (ii) The formation of a mixed anhydride (**11** in Scheme 2) was observed in the reaction between sulfoxide **4** and acetyl chloride when carried out at low temperature in the presence of one eq triethylamine. The rather unstable intermediate **11** was identified by its IR spectrum (cf. Ref.¹⁷ and Experimental part).

A similar mechanism can be proposed for the conversion of sulfoxides (*R*)-(–)-**7** and (*S*)-(+)-**9** into spiro- λ^4 -sulfanes (*R*)-(+)-**8** and (*S*)-(+)-**10**, respectively. In the latter cases, however, dehydration was carried out with DCC that can also modify the carboxyl group leading to a reactive intermediate (cf. Ref.¹²).

Here should be mentioned that the spatial structures (*R*)-(+)-**4** and (*R*)-(–)-**7** [like (*R*)-(+)-**5** and (*R*)-(+)-**8**] are not analogous although the designations of configuration are the same in both cases. In contrast with compounds **4** and **5**, the order of decreasing priority in **7** and **8** is C_{ar}(alkyl-O)→C_{ar}(acyl-O)→lone pair because the O(acyl) atom belonging to the six-membered ring B is farther from the chiral sulfur centre than the O(alkyl) atom in the five-membered ring A.



Scheme 2. The stereospecific conversion of sulfoxide $(R)\text{-}(+)\text{-4}$ into spiro- λ^4 -sulfane $(R)\text{-}(+)\text{-5}$.

The retention of sulfur configuration in the reaction $(R)\text{-}(+)\text{-4} \rightarrow (R)\text{-}(+)\text{-6}$ yielding an eight-membered sulfoxide-lactone is self-evident because the sulfinyl group does not take part in the lactone-forming dehydration of the CH_2OH and COOH groups.

Experimental

$(R)\text{-}(+)\text{-1,1'}$ -Spiro[3H-2,1-benzoxathiol]-3-one $(R)\text{-}(+)\text{-5}$

To a stirred solution of sulfoxide $(R)\text{-}(+)\text{-4}$ (2.21 g, 8 mmol, $[\alpha]_{546}^{25} = +173$, $c = 0.33$, DMF) Et_3N (1.12 mL, 8 mmol) and EtOH (0.46 mL, 8 mmol) in DMF (13 mL) was added AcCl (0.57 mL, 8 mmol) dropwise at -60°C . The stirring was continued for 20 min (-60°C), then the mixture was poured into cold (0°C) water (80 mL). The mixed anhydride of $(R)\text{-}(+)\text{-4}$ and acetic acid (see **11** in Scheme 2, cf. Ref.¹⁷) precipitated, which was immediately filtered off, washed with water then dried (2.18 g, 85%). Compound **11** was identified by its IR spectrum: ν_{max} (KBr)/ cm^{-1} 3345s (alcohol OH), 1808s and 1720s (anhydride C=O), 1004s and 995s (sulfoxide S=O).¹⁷ **11** proved to be relatively stable in solid state but decomposes rapidly in DMF solution, as shown by the change of the NMR spectrum within 20 min.

The mixed anhydride **11** (0.22 g, 0.7 mmol) was dissolved in 1,2-dichloroethane (10 mL) and the mixture was heated under reflux for 20 min then allowed to stand for 2 h at 0°C . The crystals of the starting sulfoxide $(R)\text{-}(+)\text{-4}$ (4 mg) were filtered off, then diethyl ether (30 mL) was added to the filtrate. After standing overnight at 20°C the crystals separated were filtered off, washed with diethyl ether and dried to yield spiro- λ^4 -sulfane $(R)\text{-}(+)\text{-5}$ (0.11 g, 61%, $[\alpha]_{546}^{25} = +37.5$, $c = 0.5$, DMF); mp $230\text{--}231^\circ\text{C}$; IR ν_{max} (KBr)/ cm^{-1} 1655vs (C=O), 829m (O–S–O); $^1\text{H-NMR}$ (80 MHz, CDCl_3) δ 5.60 (d, 1H, $J = 13.6$ Hz), 5.86 (d, 1H, $J = 13.6$ Hz), 7.1–8.3 (m, 8H, ArH).

$(R)\text{-}(+)\text{-5H,7H}$ -dibenzo[*c,f*]-1,5-oxathiocin-7-one 12-oxide $(R)\text{-}(+)\text{-6}$

To a stirred solution of sulfoxide $(R)\text{-}(+)\text{-4}$ (2.76 g, 10 mmol, $[\alpha]_{546}^{25} = +173$, $c = 0.33$, DMF) and Et_3N (2.8 mL, 20 mmol) in DMF (16 mL) was added AcCl (0.71 mL, 10 mmol) dropwise at -60°C . The stirring was continued for 20 min, then the mixture was poured into cold (0°C) water (80 mL). The precipitate was filtered off, washed with cold water and dried to afford sulfoxide-lactone $(R)\text{-}(+)\text{-6}$ (0.93 g, 36%, $[\alpha]_{546}^{25} = +88.3$, DMF); mp $183\text{--}185^\circ\text{C}$; IR ν_{max} (KBr)/ cm^{-1} 1739vs (C=O), 1029vs (S=O); $^1\text{H-NMR}$ (80 MHz, CDCl_3) δ 5.40 (d, 1H, $J = 13.5$ Hz), 5.84 (d, 1H, $J = 13.5$ Hz), 7.2–8.3 (m, 8H, ArH).

The mixed anhydride **11** was also converted into $(R)\text{-}(+)\text{-6}$ in the following way: 0.3 g of **11** (1 mmol) was dissolved in 1,2-dichloroethane (10 mL) containing Et_3N (0.14 mL, 1 mmol), and the mixture was heated under reflux for 20 min then evaporated to 5 mL. To the residue diethyl ether (10 mL) and hexane (25 mL) were added and allowed to stand for 2 h at 0°C . The crystals of **11** precipitated were filtered off, washed with hexane and dried (0.18 g, 70%).

(S)-(-)-Spiro[3H-2,1-benzoxathiol-1-naphtho[1,8-d,e]-3H-2,1-oxathiin-3-one] (S)-(-)-8

To a solution of sulfoxide (S)-(+)-7 (1.0 g, 3 mmol, $[\alpha]_{546}^{25}=+673$, $c=0.5$, DMF) in dichloromethane (30 mL) DCC (0.76 g, 0.37 mmol) was added and the reaction mixture was stirred for 4 h at room temperature and allowed to stand for 20 h at 4°C. The crystals of DCU were filtered off then cyclohexane (300 mL) was added to the filtrate. After standing overnight (4°C) the precipitate was filtered off, washed with pentane and dried to yield (S)-(-)-8 (0.79 g, 84%, $[\alpha]_{546}^{25}=-158$, $c=0.62$, DMF); mp 170–174°C; IR ν_{\max} (KBr)/cm⁻¹ 1628vs (C=O), 838m (O–S–O); ¹H-NMR (80 MHz, CDCl₃) δ 5.24 (s, 2H, CH₂), 7.2–8.7 (m, 10H, ArH).

(R)-(+)-Spiro[3H-2,1-benzoxathiol-1-naphtho[1,8-d,e]-3H-2,1-oxathiin-3-one] (R)-(+)-8

Spiro- λ^4 -sulfane (R)-(+)-8 ($[\alpha]_{546}^{25}=+134$, $c=0.86$, DMF) was prepared from sulfoxide (R)-(-)-7 ($[\alpha]_{546}^{25}=-575$, $c=0.5$, DMF) by a similar procedure used for the synthesis of (S)-(-)-8. The optical purity of (+)-8 was increased by crystallization from CH₂Cl₂–cyclohexane ($[\alpha]_{546}^{25}=+158$, $c=0.6$, DMF), so the physical data including the absolute values of $[\alpha]_{546}^{25}$ proved to be identical.

(S)-(+)-Spiro[3H-2,1-benzoxathiol-3-one-1-naphtho[1,8-d,e]-3H-2,1-oxathiin] (S)-(+)-10

To a solution of sulfoxide (S)-(+)-9 (0.33 g, 1 mmol, $[\alpha]_{546}^{25}=145$, $c=0.5$, DMF) in dichloromethane (20 mL) DCC (0.25 g, 1.2 mmol) was added and the mixture was stirred for 4 h at room temperature. DCU was filtered off and the filtrate was evaporated to 5 mL, then mixed with pentane (10 mL). After standing overnight the crystals separated were filtered off, washed with pentane and dried to give (S)-(+)-10 (0.23 g, 75%, $[\alpha]_{546}^{25}=+852$, $c=0.41$, DMF); mp 220–222°C; IR ν_{\max} (KBr)/cm⁻¹ 1678vs (C=O), 825m (O–S–O); ¹H-NMR (80 MHz, CDCl₃) δ 5.45 (d, 1H, J=15.6 Hz), 5.99 (d, 1H, J=15.6 Hz), 7.2–8.4 (m, 10H, ArH).

Single crystal X-ray diffraction analysis

X-Ray data were recorded on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Cu K α ($\lambda=1.54184$ Å) radiation for (R)-(+)-5 and (R)-(+)-6 by using ω -2 θ scan in the range $3.5^\circ < \theta < 77.0^\circ$ at room temperature (293 K), whereas data for (R)-(+)-8 were collected with Mo K α ($\lambda=0.71073$ Å) in the range $2.75^\circ < \theta < 40.1^\circ$ at low temperature (130 K). Cell constants for each crystal were determined by least squares refinement of diffractometer angles for 25 automatically centred reflections. For each crystal three standard reflections were monitored every hour. No decay correction was applied in either case. Intensities were corrected for Lorentz and polarization effects. The phase problems were solved by direct methods by using the program SHELXS86.²⁶ Full matrix least-squares refinement minimized $\sum w(\Delta F^2)^2$ for the all unique reflections by the program SHELXL93²⁷ with the weighting scheme: $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ (where $P=[\text{Max}(F_o^2,0)+2F_c^2]/3$ while a and b varied for each data set). In each case, the fractional coordinates of the hydrogen atoms were generated from assumed geometries and were constrained to the corresponding heavy atoms with isotropic displacement parameters. Because compounds crystallized with a polar space group Flack parameter²⁸ was refined for each structure. However, the Flack parameter calculated from data collected with Mo K α at low temperature for (R)-(+)-8 has been checked by using reflections with strong sulfur contribution.

(R)-(+)-5

C₁₄H₁₀O₃S, $M_r=258.28$, orthorhombic, space group $P2_12_12_1$, $a=8.636(2)$, $b=9.458(1)$, $c=14.375(3)$ Å, $V=1174.1(4)$ Å³, $Z=4$, $D_c=1.461$ Mg.m⁻³, $F(000)=536$, $\mu=2.435$ mm⁻¹. Crystal (mm): 0.30×0.25×0.12 (from dichloromethane–acetone). 2364 independent reflections [$R(\text{int})=0.027$] measured. Final $R=0.084$, $wR=0.246$ for 2340 reflections applied in the refinement, $R' = 0.100$ and $wR' = 0.259$ for all observations which can be attributed to the positional disorder exhibited by the oxygen atom pertaining to the carbonyl moiety. GOF=1.051. Absolute structure parameter 0.03(5).

(R)-(+)-6

$C_{14}H_{10}O_3S$, $M_r=258.28$, monoclinic, space group $P2_1$, $a=4.761(1)$, $b=12.941(1)$, $c=9.645(1)$ Å, $\beta=101.06(1)^\circ$, $V=583.16(4)$ Å³, $Z=2$, $D_c=1.471$ Mg.m⁻³, $F(000)=268$, $\mu=2.451$ mm⁻¹. Crystal (mm): $0.40\times 0.30\times 0.15$ (from dichloromethane–hexane). 2425 independent reflections [$R(\text{int})=0.037$] measured. Final $R=0.034$, $wR=0.088$ for 2417 reflections applied in the refinement, $R'=0.034$ and $wR'=0.089$ for all observations, GOF=1.134. Absolute structure parameter 0.00(2).

(R)-(+)-8

$C_{18}H_{12}O_3S$, $M_r=308.34$, orthorhombic, space group $P2_12_12_1$, $a=8.654(1)$, $b=10.750(1)$, $c=14.312(1)$ Å, $V=1331.5(2)$ Å³, $Z=4$, $D_c=1.538$ Mg.m⁻³, $F(000)=640$, $\mu=0.254$ mm⁻¹. Crystal (mm): $0.13\times 0.18\times 0.35$ (from dichloromethane–cyclohexane). 8266 independent reflections [$R(\text{int})=0.038$] measured. Final $R=0.050$, $wR=0.107$ for 8265 reflections applied in the refinement, $R'=0.116$ and $wR'=0.129$ for all observations, GOF=1.008. Absolute structure parameter 0.03(7).

Supplementary data for the X-ray crystallographic studies on (R)-(+)-5, (R)-(+)-6, and (R)-(+)-8 including bond lengths and angles have been deposited with the director of the Cambridge Crystallographic X-ray Database and they are available on request.

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