Chromatographic Resolution, Circular Dichroism Spectra, Absolute Configurations, and Crystal Structures of Bridged Biphenyls, Containing Sulfide, Sulfoxide, and Sulfone Groups in the Bridge

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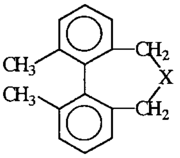
Dedicated to Prof. *Albrecht Mannschreck*, University of Regensburg

Four chiral 1,1′-biphenyls with one or two sulfur-containing bridges in 2,2′- or 2,2′- and 6,6′-positions, *viz.* 1,11-dimethyl-5,7-dihydrodibenzo[*c,e*]thiepin (**1**), its *S*-oxide (**2**) and *S,S*-dioxide (**3**), and the doubly bridged 10,12-dihydro-4*H*,6*H*-[2]benzothiepino[6,5,4-*def*][2]benzothiepin (**4**) have been studied by chromatography, CD spectroscopy, X-ray crystallography, and empirical force-field and CNDO/S calculations. The structures obtained by force-field calculations showed good agreement with the crystal structures determined for **2** and **3**. Compounds **2**, **3**, and **4**, but not **1**, could be resolved into enantiomers by chromatography on swollen microcrystalline triacetylcellulose. The barrier for biphenyl inversion in **2** was found to be higher than 167 kJ · mol^{-1} by an attempted thermal racemization. The CD spectra of the enantiomers of **2**–**4** were recorded and resolved into individual bands, and the corresponding rotational strengths were calculated. The transitions showed considerable similarity to those of a 1,1′-biphenyl with hydrocarbon bridge (*cf.* **5**), albeit with bathochromic shifts, which permitted the assignment of the absolute configurations of the enantiomers of **2**–**4**. The assignments were supported by comparison of the experimental CD spectra with spectra calculated by the CNDO/S method. All first-eluted enantiomers were found to have the (*S*)-configuration.

Introduction. – Bridged biphenyls have played an important role in organic stereochemistry [1–3], notably in studies of the chiroptical properties of the biphenyl system [4]. The electronic transitions in biphenyls have been studied by UV and CD spectra, and by semiempirical calculations [5–8]. The present study deals with bridged biphenyls containing sulfide, sulfoxide, and sulfone functions in the bridge, and it was undertaken in order to investigate the importance of these groups for the geometry of the biphenyl system and the effects of interactions between the biphenyl and sulfur chromophores on the CD spectra. The compounds chosen for the study are 1,11-dimethyl-5,7-dihydrodibenzo[*c,e*]thiepin (**1**), its *S*-oxide (**2**) and *S,S*-dioxide (**3**), and 10,12-dihydro-4*H*,6*H*-[2]benzothiepino[6,5,4-*def*][2]benzothiepin (**4**). Suitable reference compounds are found among hydrocarbon-bridged biphenyls, *e.g.*, **5** [8].

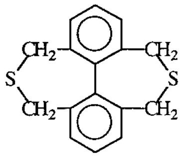
Chromatography on triacetylcellulose as a chiral stationary phase has earlier been found useful for separation of enantiomers of bridged biphenyls and has also been performed for the present systems. Since the geometry and, in particular, the dihedral



1 X = S

2 X = SO

3 X = SO_2



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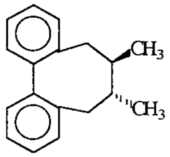

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angle between the Ph rings is of importance for the spectroscopic properties of these compounds, crystallographic studies and empirical force-field calculations were also performed.

Experimental. – *Materials.* Compounds **1** and **4** have been described by *Mislow et al.* [4], and **2** and **3** by *Frazer* and *Schuber* [9]. Our syntheses were performed mainly according to these procedures, but the key intermediate 6,6′-dimethyl-[1,1′-diphenyl]-2,2′-dicarboxylic acid was prepared *via* the diazonium salt of 3-methylanthranilic acid [10]. All compounds were obtained as colorless crystals. The dihydrodibenzothiepin **1** was obtained as prisms (m.p. 100–101° ([4]: 102–103°)). Single crystals of the sulfoxide **2** for X-ray crystallographic analysis were grown by slow evaporation of a cyclohexane soln. (m.p. 137–138° ([9]: 137–138°)). In spite of numerous attempts, crystals of better quality could not be obtained. The sulfone **3** was obtained as good crystals (m.p. 221–222° ([9]: 221–222°)) by recrystallization from acetone. Crystals of **4** (m.p. 266–268° ([4]: 266–267°)) were grown by slow crystallization from acetone soln., but despite many attempts, it was not possible to obtain crystals suitable for crystallographic analysis.

Instruments and Measurements. The crystallographic unit-cell parameters for compounds **2** and **3** were determined by a least-squares fit of 19 and 17 peak maxima, resp. (2Θ in the range 15–34°). The usual corrections were applied for *Lorentz* and polarization effects, but not for absorption. Detailed crystal and refinement data are shown in *Table 1.*

The structures were solved by direct methods and were refined by the full-matrix least-squares technique. H-Atoms were allowed to ride on the attached atoms. The Ph rings in **2** were refined as regular hexagons, and all C-atoms were refined isotropically because of the poor reflections-to-parameters ratio (429 observed reflections). The function minimized was $\Sigma\,\omega(|F_o|-|F_c|)^2$, where the weighting factor is $\omega=[\sigma^2(F_o)+g\,F_o^2]^{-1}$. The program SHELXS86 [11] and the CHRYSRULER package [12] were used to solve and refine the structures. The programs CSU [13] and SHELXL93 [14] were used for preparing CIF files for the *Cambridge Structural Database.* The numbering of the non-H-atoms in **2** and **3** is shown in *Fig. 1.* The crystals of both **2** and **3** are centrosymmetric (*R*/*S*), and stereoscopic views of the (*S*)-enantiomers are shown in *Fig. 2,a* and *b.*

The stereoplots were drawn with the program PLUTON-89 [15]. Selected bond lengths, bond angles, and dihedral angles are given in *Table 2* (CSD deposition numbers: 130255 for **2**, and 130256 for **3**).

Chromatography with swollen microcrystalline triacetylcellulose (TAC) [16] has been described by *Isaksson* and *Roschester* [17]. The compounds (*ca.* 1 mg) were dissolved in EtOH (1 ml), injected into the chromatography system (*Conbrio*-TAC column [18]), and eluted with EtOH/H_2O 95:5. Detection was performed by UV (225 nm) and polarimetry (365 nm). Compound **1** could not be resolved, but compounds **2** and **4** (*Fig. 3*) could be reasonably separated, and pure enantiomers were obtained after recycling twice and once, respectively.

Compound **3** showed more overlapping of the chromatographic peaks, and samples of 70% ((−)-**3**) and 35% ((+)-**3**) ee were used in the CD studies. The ee value was determined by recording the ^{1}H-NMR spectra of racemic and optically active samples containing (+)-[Eu(hfb)$_3$] [19–21]. The analysis was based on the resonances of the diastereotopic Me groups, and their relative intensities were assessed by simulation with *Lorentzian* curves. Capacity and selectivity factors [22] for the separation of **2**–**4** are listed in *Table 3.* It is worth noting that the (−)-form is eluted first for all three compounds.

Table 1. *Crystallographic Data for Compounds* **2** *and* **3**

Compound	**2**	**3**
Formula, formula weight	$C_{16}H_{16}OS$, 256.4	$C_{16}H_{16}O_2S$, 272.4
Color	Colorless	Colorless
Crystal size [mm]	0.40 × 0.30 × 0.05	0.28 × 0.43 × 0.60
Space group	*Pbcn*, orthorhombic	$P2_1/c$, monoclinic
a [Å]	15.534(6)	7.014(1)
b [Å]	17.774(20)	13.250(4)
c [Å]	9.648(2)	15.101(8)
α [°]	90.00	90.00
β [°]	90.00	91.10(2)
γ [°]	90.00	90.00
Volume [Å^3]	2664(3)	1403.2(9)
Z	8	4
Density (calc., Mg/m^3)	1.279	1.289
Absorption coefficient (cm^{-1})	0.217	0.215
F (000)	1088	576
Diffractometer	*PW1100* (*STOE* upgrade)	
Radiation	MoK_α ($\lambda = 0.71073$ Å)	
Monochromator	Graphite crystal	
2Θ Range [°]	4 to 54	4 to 60
Scan type	ω	
Scan range [°] (plus K_α)	1.25	1
Standard reflections (measured every 100 min)	(2,2,1) (−2,−2,−2) (2,4,1)	(2,3,2) (−2,0,8)
Index ranges	0,16; 0,17; 0,10	−9,9; 0,17; 0,21
Independent reflections	2917 [$429 \geq 2\sigma(I)$]	3990 [$1774 \geq 2\sigma(I)$]
Number of parameters	51	175
Final *R*, R_w	0.078, 0.087	0.050, 0.054
$(\Delta/\sigma)_{max}$	0.014	0.007
S	3.104	1.010
Residual peaks [e · Å^{-3}]	−0.24, 0.35	−0.35, 0.24
g (weighting scheme)	0.00069	–

UV Spectra were recorded with a *Cary Model 2290* spectrophotometer (0.1-cm cells) and CD spectra in general with a *JASCO Model J-500A* spectropolarimeter. The CD spectrum of **5** was recorded on a *JASCO Model J-720A* spectropolarimeter (courtesy of *JASCO Ltd.*, Japan).

Samples from chromatography were evaporated and dissolved to suitable concentrations in spectroscopic-grade MeCN before recording UV and CD spectra. The concentrations were monitored by comparison of the UV spectra with spectra measured with solns. of the racemates with known concentrations. The spectra of the first- and second-eluted enantiomers showed good mirror-image behavior. UV and CD spectral data are shown in *Table 4*.

The experimental spectra were digitalized and simulated by sets of *Gaussians*, according to a least-squares approach [23]. In all cases, quite good agreement with the experimental curves was obtained. From the *Gaussians*, the rotational strengths of the transitions (R_i, in D × μ_B) were obtained by *Eqn. 1*, where Δ_e is half the bandwidth at $\varepsilon = \Delta\varepsilon_{max}/e$.

$$R_i = 0.4389 \cdot \Delta\varepsilon_{max} \Delta_e / \lambda_{max} \qquad (1)$$

The data obtained by resolution of the CD spectra of (−)-**2**, (−)-**3**, and (−)-**4** are shown in *Table 5*.

Samples of optically pure (+)-**2** in diglyme were placed in thick-walled glass ampoules, the soln. was deoxygenated with N_2, and the ampoules were sealed. The ampoules were kept at selected temps. for a few hours, cooled, and opened, whereupon the CD spectrum was recorded. Not even after prolonged heating at 220° was any change in the UV or CD spectrum observed, indicating that neither ring inversion nor thermal decomposition had taken place. This allows the estimation of a lower limit of the inversion barrier of 167 kJ · mol^{-1}.

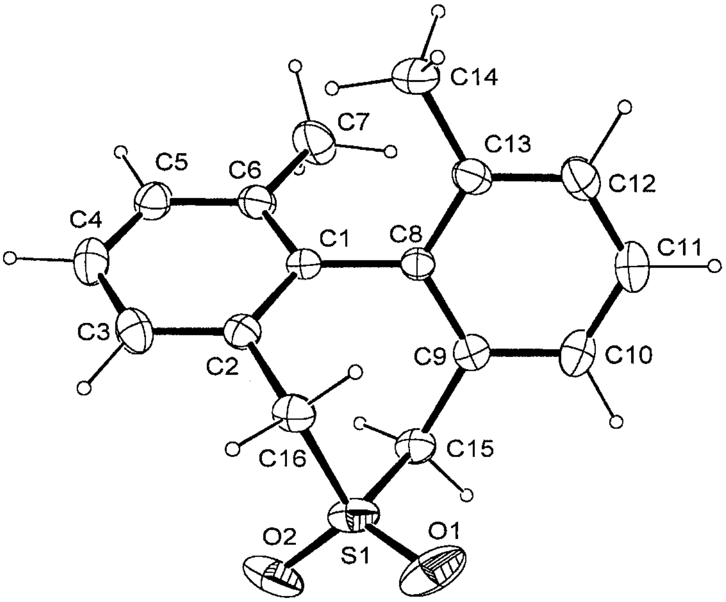

Fig. 1. *Numbering for (*S*)-***3**. The same numbering is, *mutatis mutandis*, valid for the other compounds.

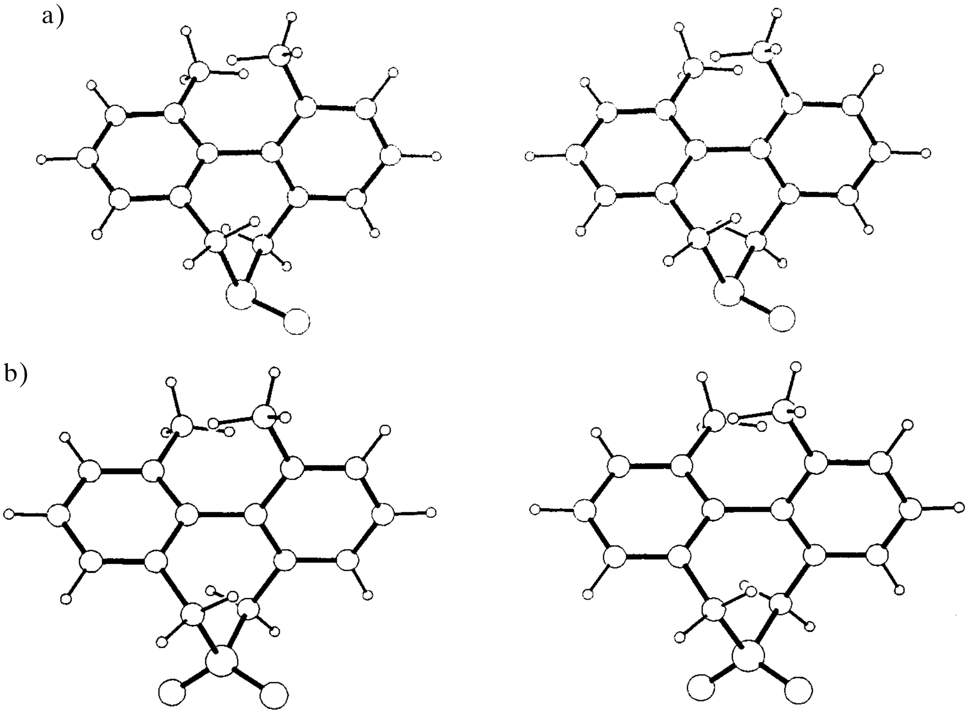

Fig. 2. a) *Stereoscopic view of the crystal structure of* **2** ((*S*)-enantiomer represented). b) *Stereoscopic view of the crystal structure of* **3** ((*S*)-enantiomer represented).

Table 2. *Bond Lengths, Bond Angles, and Dihedral Angles in* (R)-**2**, (R)-**3**, *and* (R)-**4** *by X-Ray Crystallography* (**2** and **3**) *and by MM2-91 Calculations* (for numbering, see *Fig. 1*)

Compound	**2**		**3**		**4**
	X-Ray	MM2	X-Ray	MM2	MM2
Bond length [Å]					
S(1)−O(1)	1.500(19)	1.480	1.452(4)	1.450	–
S(1)−O(2)	–	–	1.448(4)	1.450	–
S(1)−C(15)	1.832(15)	1.809	1.797(4)	1.791	1.817
S(1)−C(16)	1.829(16)	1.809	1.787(4)	1.791	1.817
C(1)−C(2)	1.396(14)	1.405	1.411(5)	1.406	1.404
C(1)−C(6)	1.394(15)	1.404	1.403(5)	1.404	1.404
C(1)−C(8)	1.496(14)	1.496	1.498(5)	1.498	1.491
C(2)−C(16)	1.445(18)	1.510	1.513(5)	1.510	1.511
C(6)−C(7)	1.492(17)	1.510	1.523(6)	1.511	1.511
C(8)−C(9)	1.395(15)	1.405	1.405(5)	1.405	1.404
C(8)−C(13)	1.395(16)	1.405	1.411(5)	1.404	1.404
C(9)−C(15)	1.498(18)	1.511	1.510(5)	1.510	1.511
C(13)−C(14)	1.505(19)	1.511	1.521(6)	1.511	1.511
Bond angle [°]					
C(15)−S(1)−C(16)	97.5(7)	99.3	104.3(2)	105.0	100.5
O(1)−S(1)−C(15)	106.0(8)	107.1	109.1(2)	108.8	–
O(1)−S(1)−C(16)	107.9(8)	106.8	107.4(2)	108.5	–
O(2)−S(1)−C(15)	–	–	107.4(2)	108.4	–
O(2)−S(1)−C(16)	–	–	109.6(2)	108.8	–
O(2)−S(1)−O(2)	–	–	118.1(2)	116.7	–
Dihedral angle [°]					
O(1)−S(1)−C(15)−C(9)	+64.8(1.2)	+67.8	+70.1(4)	+72.0	–
O(1)−S(1)−C(16)−C(2)	−154.6(1.1)	−157.9	−160.9(3)	−159.7	–
O(2)−S(1)−C(15)−C(9)	–	–	−158.8(3)	−160.1	–
O(2)−S(1)−C(16)−C(2)	–	–	+71.6(3)	+72.4	–
C(2)−C(1)−C(8)−C(9)	−63.1(1.3)	−58.5	−62.6(5)	−61.1	−55.2
C(2)−C(1)−C(8)−C(13)	+116.5(1.2)	+118.0	+116.5(4)	+116.2	+124.8
C(6)−C(1)−C(8)−C(9)	+118.0(1.2)	+118.2	+115.9(4)	+116.2	+124.8
C(6)−C(1)−C(8)−C(13)	−62.5(1.5)	−65.4	−65.0(5)	−66.5	−55.2
C(1)−C(8)−C(13)−C(14)	−3.5(1.7)	−2.7	−7.3(6)	−3.0	−2.3
C(8)−C(1)−C(6)−C(7)	−6.5(1.7)	−2.8	−6.3(6)	−2.9	−2.3

Table 3. *Chromatographic Data for* **1**–**4**

Compound	k'_1	k'_2	α	Φ[a])
1	1.6	1.6	1.0	±
2	1.3	3.2	2.5	–
3	3.8	5.2	1.4	–
4	3.9	8.5	2.2	–

[a]) Sign of rotation of the first-eluted enantiomer at 365 nm.

Theoretical Calculations. The structures of compounds **1**–**4** were constructed and analyzed with the MacMimic implementation [24] of the *Allinger* MM2-91 force field [25][26]. CNDO/S Calculations were performed with a program based on the original *Jaffé* formalism but modified for sulfur compounds [27] and for calculations of CD spectra [28]. Two-center repulsion integrals were calculated by the *Nishimoto-Mataga* formalism [29], and configuration interaction was performed with the 50 lowest singly excited states. Inclusion of a larger number of configurations was considered unnecessary, since it has only a moderate effect on the

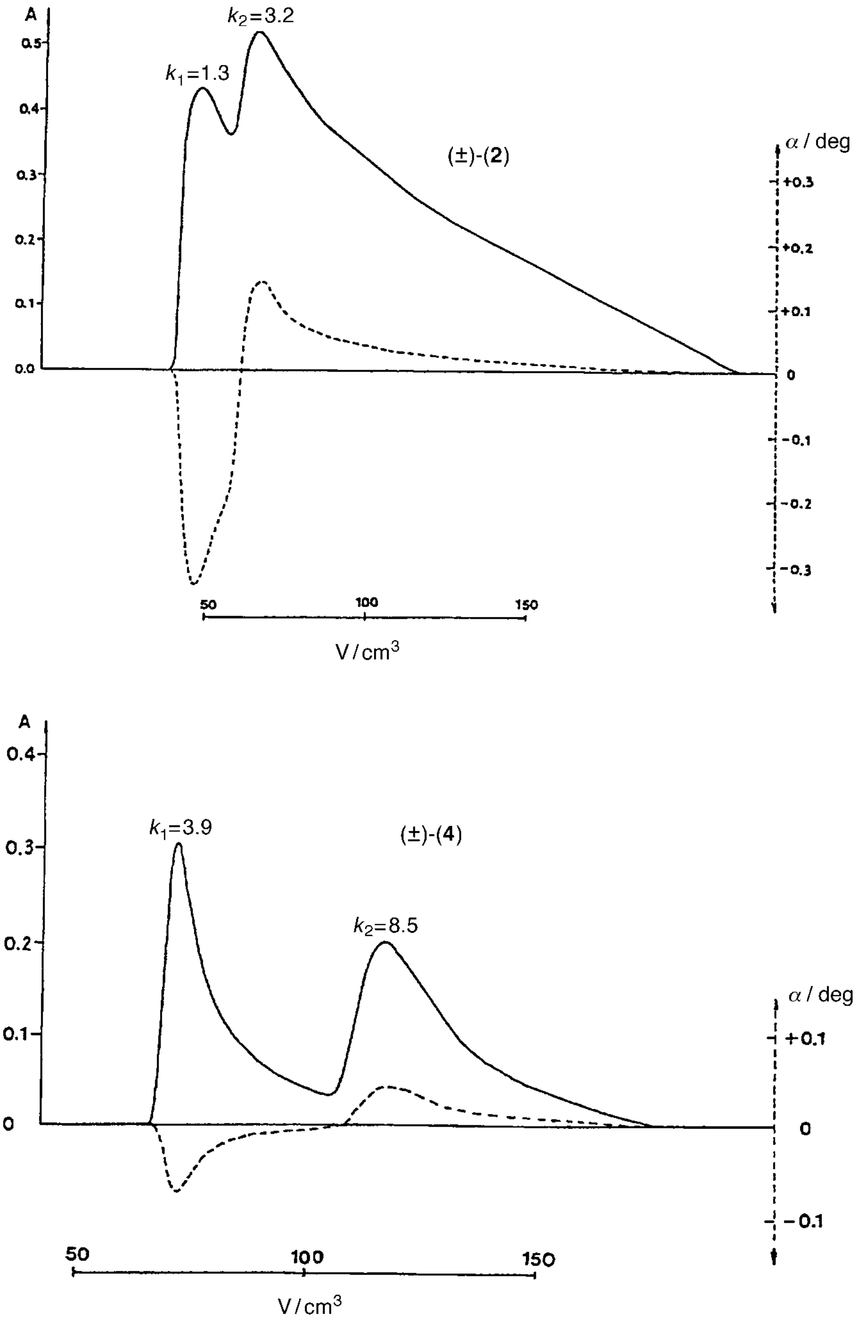

Fig. 3. *Chromatograms of* **2** *and* **4**

Table 4. *UV and CD Spectra of Compounds* **2**–**5**. CD Spectra are of the first-eluted enantiomers. Solvent for **2**–**4**, MeCN, and for **5**, hexane.

Compound		λ [nm] (ε, $\Delta\varepsilon$ [$\mathrm{M}^{-1}\cdot\mathrm{cm}^{-1}$])
5	UV	273 (500), 263 (1000), 235 (12000), 212 (44000), 208 (44500), 179 (32000)
	CD	275 (– 0.56), 268 (– 0.85), 235 (– 24.0), 218 (– 46.6), 201 (+ 58.7), 188 (+ 94.7), 176 (– 83)
2	UV	250 (sh [a])) (3300), 219 (42000), 190 (41000, end absorption)
	CD	285 (sh) (– 2.6), 260 (– 27.9), 231 (– 34.0), 204 (+ 102), 200 (+ 108), 187 (– 113)
3	UV	279 (sh) (1300), 27 (2240), 240 (sh) (7500), 217 (39500), 190 (45000, end absorption)
	CD	283 (– 2.8), 273.5 (– 2.3), 241 (– 44.6), 222 (– 55.0), 209 (sh) (+ 132), 200 (+ 227), 188 (– 102)
4	UV	287 (sh) (1200), 238 (sh) (6800), 207 (29500), 190 (43000, end absorption)
	CD	292 (– 6.9), 256 (– 39.9 [b])), 229 (+ 35.3), 206 (+ 51), 189 (– 60)

[a]) Shoulder. [b]) Resolved into two *Gaussians* with $\lambda_{\max}$ 242 nm ($\Delta\varepsilon$ – 10.5) and 255 nm ($\Delta\varepsilon$ – 35.5), see also *Table 5*.

calculated transition energies and oscillator and rotational strengths, and it complicates the analysis of the transitions in terms of molecular orbitals. The theoretical CD spectra were obtained from the calculated R_i and $\lambda_{\max,i}$ values as sums of *Gaussians* by *Eqn. 2*, in which the Δ_e values were mean values from the resolution of the experimental CD spectra in the respective wavelength regions.

$$\Delta\varepsilon = \Sigma\, \Delta\varepsilon_{\max} \cdot \exp\{-[(\lambda - \lambda_{\max})/\Delta_e]^2\} \qquad (2)$$

Results and Discussion. – *Crystal Structures and Force-Field Calculations.* The crystal structures of **2** and **3** (*Table 2*) show quite similarly twisted biphenyl moieties with dihedral angles (Θ) in the range of 60 to 65°. Calculations for **2** and **3** by the MM2-91 force field generally reproduce the crystal structures quite well. The most notable difference is found for the length of the C(2)–C(16) bond in **2**, but here the calculated bond length is the more credible one. Obviously, the MM2 geometry for **4** can be used with confidence for the calculation of its CD spectrum. According to MM2 calculations, **1** and **3** have C_2 symmetry, while **2** has C_1 and **4** has D_2 symmetry. In the crystal, the molecule of **3** has C_2 pseudosymmetry.

The interaction between the two Me groups at C(6) and C(13) (the C(7)–C(14) distance is 3.311 Å in **2**, 3.426 Å in **3**) leads to small deviations from planarity of the benzene rings. This interaction is largely responsible for the fairly large twist angle, since Θ for **1** is predicted to be in the range 60 to 65°, as found by crystallography for **2** and **3**, while for the analogue without Me groups, it is predicted to be 52°, not very different from the 55° predicted for **4**. The long C–S bonds and the narrow C–S–C angle in the CH_2SCH_2 bridge also influence the twist angle, since Θ for the analogue with a $CH_2CH_2CH_2$ bridge and without Me groups is predicted to be only 47°.

UV and CD Spectra. The electronic transitions in compounds **2**–**4** can be discussed in relation to the transitions in biphenyls with saturated hydrocarbon 2,2′-bridges and similar twist angles. A suitable reference compound is *trans*-5,6,7,8-tetrahydro-6,7-dimethyldibenzo[*a*,*c*]cyclooctene (**5**). According to X-ray crystallography [7] and force-field calculations [30], biphenyls with a saturated C_4 bridge predominantly assume a twist-boat-chair (TBC) conformation with a Θ value of *ca.* 60°. *trans*-Related substituents at C(6) and C(7) undergo e,e/a,a exchange by inversion of the eight-membered ring (and the biphenyl system) with free-energy barriers in the range of 95–102 kJ · mol^{-1} but prefer the *e*,*e*-conformation. According to NMR spectra at 298 K in

Table 5. *Data from the Resolution of the CD Spectra of Compounds* **2**–**5**. The rotational strength ***R*** is given in $\mathrm{D}\cdot\mu_\mathrm{B}$. $1\ \mathrm{D}\cdot\mu_\mathrm{B} = 3.0917\cdot10^{-53}$ SI units $= 9.2741\cdot10^{-39}$ *cgs* units.

Transition	**2**				**3**				**4**				**5**				Polarization
	$\Delta\varepsilon$	Δ_e [nm]	λ [nm]	R	$\Delta\varepsilon$	Δ_e [nm]	λ [nm]	R	$\Delta\varepsilon$	Δ_e [nm]	λ [nm]	R	$\Delta\varepsilon$	Δ_e [nm]	λ [nm]	R	
1	−1.5	5.0	289.5	−0.011	−2.7	7.0	282	−0.029	−7.0	12.0	292	−0.126	−1.6	4.3	273	−0.011	x
					−2.3	7.0	273	−0.026					−2.1	4.4	263	−0.015	z
2	−28.1	15.1	260.0	−0.72	−43.4	9.7	240.5	−0.77	−35.5	11.5	255	−0.70	−24.5	11.3	234.5	−0.52	y
3	−34.2	5.5	229.5	−0.36	−52.5	4.8	222.0	−0.50	−10.5	7.3	242	−0.14	−40.5	7.0	216	−0.58	x
4	+92.8	11.0	206.5	+2.17	+115.9	5.1	208.5	+1.24	+34.9	7.0	229.5	+0.47	+70.0	8.0	204	+1.20	z
5	+60.3	5.1	198	+0.68	+221.9	6.0	199.5	+2.93	+51.0	11.4	205.5	+1.24	+95.0	7.0	189	+1.54	y
6	−106.7	4.8	187	−1.20	−106.8	4.9	188.5	−1.22	−59.0	5.5	199	−0.75	−83.0	7.0	176	−1.45	x

Table 6. *Experimental and Calculated* (CNDO/S) *Band Maxima* ([nm])

Transition	**2**		**3**		**4**		**5**	
	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.
1 [a])	289.5	286.7	282	286.6	292	287.5	273	276.7
2	260	258.3	240	246.9	255	260.2	234.5	245.3
3	229.5	214.0	222	215.7	242	239.8	216	209.3
4	206.5	206.8	208.5	212.3	229.5	224.6	204	193.4
5	198	229.6	199.7	228.4	205.5	192.2	189	183.8
6	187	190.2	188.5	188.7	190	187.7	176	178.7

[a]) The long-wavelength band.

$CDCl_3$, **5** exists to 93% in the *e*,*e*-conformation. Therefore, the diastereoisomer with (*R*,*R*)-configuration at C(6) and C(7) has predominantly (*S*)-configuration of the biphenyl unit.

The UV spectra of *trans*-6,7-disubstituted 5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctenes are rather similar with one or two weak bands in the range 260–280 nm, assigned [6] to combinations of the ^1L_b transitions (in the nomenclature of *Platt* [31]), followed by one band of medium intensity at *ca.* 235 nm, the A band of *Suzuki* [32][33], the position of which is strongly dependent on Θ. A stronger band, in some spectra with two maxima, appears at *ca.* 210 nm, and the UV spectrum of **5**, which has been recorded in the range 168–300 nm [34], displays a further strong band at 179 nm. The CD spectrum of the (*S*)-enantiomer of **5** (*Fig. 4* and *Table 4*) shows two weak, negative bands at 273 and 265 nm, followed by a stronger negative A band at 232 nm. Two strong bands appear at 217 (negative) and 202 nm (positive), and still stronger bands are observed at 195 nm (positive) and 175 nm (negative). This spectrum was qualitatively reproduced by a CNDO/S calculation (*Fig. 4*).

The CD spectra of the first-eluted enantiomers of **2** (*Fig. 5*), **3** (*Fig. 6*), and **4** (*Fig. 7*) show striking resemblance to that of (*S*)-**5**, although with the bands bathochromically shifted to varying extent.

These shifts may be ascribed to differences in Θ, to hyperconjugation of the methyl groups, and to interaction between the biphenyl unit and the chromophores in the bridge(s). This interaction can be regarded as a homoconjugation, extending the delocalized system. Besides bathochromic shifts, the homoconjugation leads to

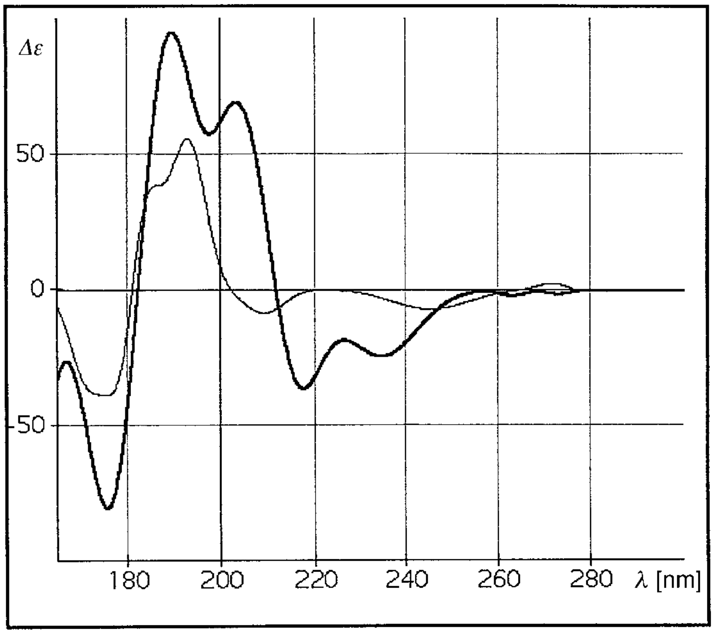

Fig. 4. *Experimental* (**—**, in hexane) *and theoretical* (—) *CD spectrum of* **5**

enhancements of the electric transition moments of both the biphenyl-chromophore and the bridge-chromophore transitions with concomitant strengthening of the CD bands. On the other hand, through-space couplings of the biphenyl transitions with the bridge-chromophore transitions by the coupled oscillator mechanism [35] gives couplets, which may add to or detract from the intensities of the CD bands, depending on the spatial orientation of the transition moments involved. The rotational strength generated by coupling between two non-degenerate transitions A and B in separate chromophores is approximately given by *Eqn. 3* [36], where V_{AB} is the energy of coupling between the transitions, ν_A and ν_B are the transition energies, R_{BA} is the distance vector between the centers of the chromophores, and μ_A and μ_B are the transition moments.

$$\boldsymbol{R}_{A,B} = \pm 2\pi \cdot V_{AB} \cdot \nu_A \cdot \nu_B \cdot [R_{BA} \cdot \mu_B \times \mu_A]/h\,c(\nu_B^2 - \nu_A^2) \qquad (3)$$

For discussion, the transitions and the corresponding bands are numbered, starting from low energies, with assignments, polarizations (*Fig. 8*), and predicted signs for the (*S*)-enantiomer: *1*) the ^1L_b transition combinations (x, $+$, and z, $-$); *2*) the A-transition (the in-phase ^1L_a combination) [6], polarized along the long axis of the biphenyl chromophore (y, $-$); *3*) the first ^1B_b combination, according to CNDO/S calculations perpendicular to the long axis and bisecting the smaller dihedral angle between the phenyl groups (x, $-$); *4*) a second ^1B_b combination, according to CNDO/S calculations perpendicular to the long axis and bisecting the larger dihedral angle between the phenyl groups (z, $+$); *5*) a transition of ^1B_a-type combination, polarized

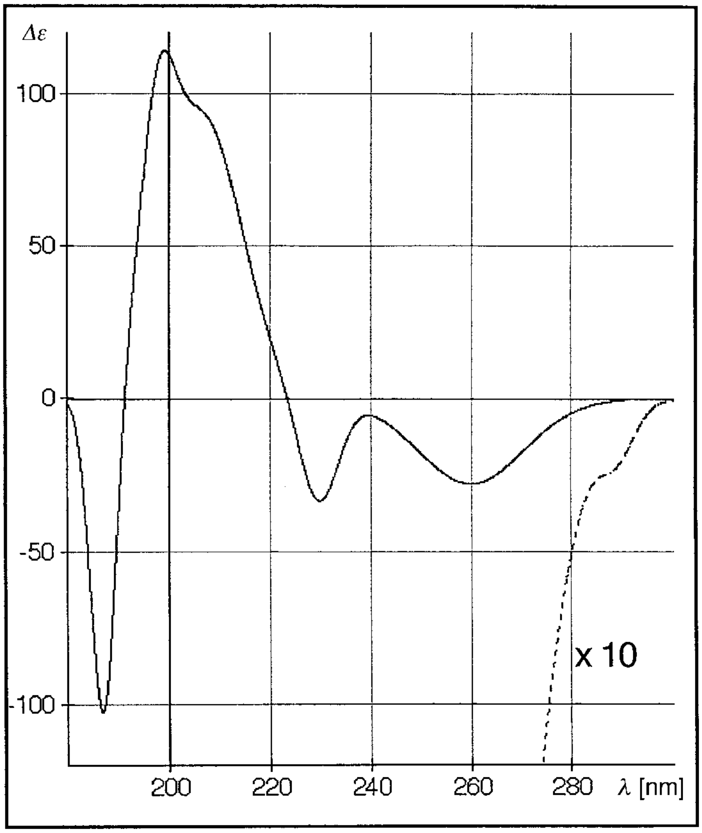

Fig. 5. *CD Spectrum of (*S*)-**2** in MeCN*

along the long axis (*y*, +); and *6*) a third ^1B_b-type combination, according to CNDO/S calculations polarized perpendicular to the long axis and bisecting the larger dihedral angle between the Ph groups (*x*, −).

The data in *Table 5* show that compound **3** displays the smallest red-shifts of bands 1–3. The rotational strengths, except for band 5, show only moderate changes compared to those of (*S*)-**5**. The $CH_2SO_2CH_2$ chromophore has no selective absorption above 180 nm, and it is therefore reasonable to assume that the wavelength shifts and changes in rotational strengths are mainly due to the effects of the Me and CH_2 substituents in the biphenyl moiety. The absolute configuration of (−)-**3** can with confidence be assigned as (*S*).

The CD spectrum of **2** shows larger red shifts of bands 1–3 and also more notable differences in band intensities. Band 3 shows diminished and band 4 strongly increased intensity. This may be ascribed to low-lying transitions in the $CH_2S(O)CH_2$ chromophore. UV Spectra of simple sulfoxides show three bands of low-to-medium intensity in the wavelength range 230–170 nm. The first transition, SO-1, gives rise to a band in the range 220–230 nm with ε of *ca.* 1000. According to *ab initio* SCF

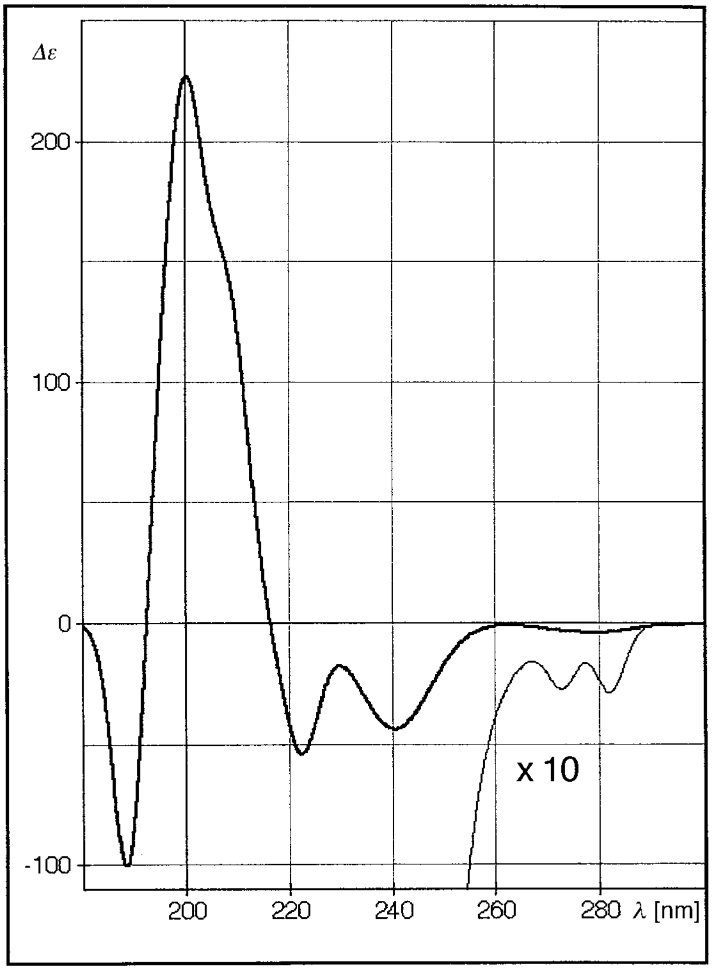

Fig. 6. *CD Spectrum of (*S*)-**3** in MeCN*

calculations with extensive configuration interaction [37], this transition is polarized perpendicular to the plane which lies in the S–O bond and bisects the C–S–C angle. SO-1, lying close to transitions 2 and 3, is the best candidate for strong interactions with these transitions through the coupled oscillator mechanism [35]. The dihedral angle between the transition moments of 2 in (*S*)-**2** and SO-1 is – 64.0° (*Fig. 9*), which should lead to a contribution of negative couplet character, centered at *ca.* 235 nm.

This is in accord with the strengthening of the negative band 2 and the weakening of the likewise negative band 3 of (–)-**2** compared to that of (*S*)-**5**. Transition 3 is perpendicular to the SO-1 transition, and the interaction between them gives no contribution through the coupled oscillator mechanism. The polarizations of the following SO transitions are not known, but it seems possible that the strengthening of band 4 and weakening of band 5 have their origin in a second couplet contribution

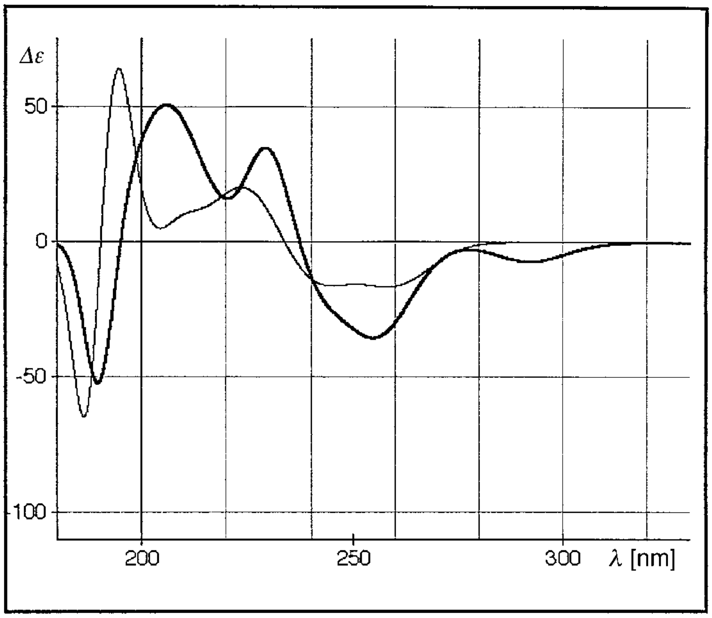

Fig. 7. *Experimental* (—, in MeCN) *and theoretical* (—) *CD spectrum of* (S)-**4**

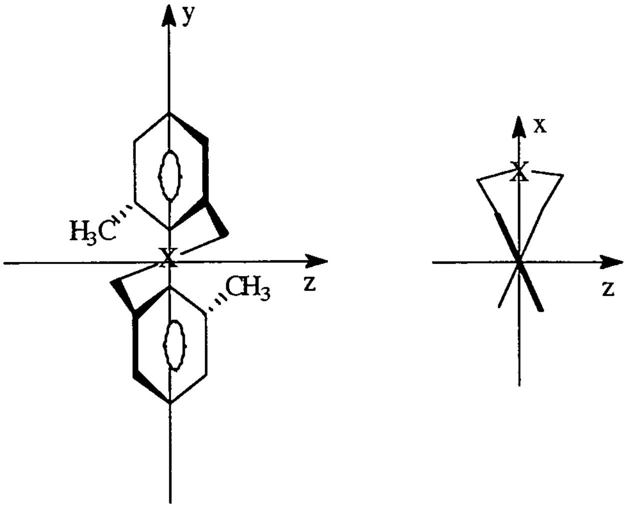

Fig. 8. *Polarization coordinates for* (S)-*enantiomers*

involving SO-2, situated near 200 nm. Also for (−)-**2**, we can confidently assign the absolute configuration as (*S*).

The CD spectrum of (−)-**4** (*Fig. 7*) is similar to the previous ones in general appearance, notable differences being the increased intensity of band 1 and the strong

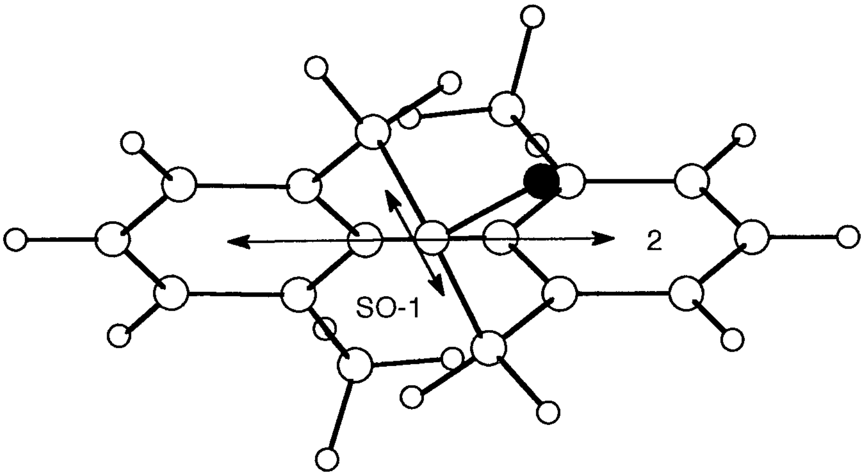

Fig. 9. *Transition-Moment Directions for SO-1 and Transition 2 in (*S*)-***2**

bathochromic shifts of all bands. Part of the differences may be due to the smaller dihedral angle Θ (55° compared to 60–65° for **2** and **3**) and to interactions between the biphenyl and CH_2SCH_2 chromophores. Band 2 is shifted by 20 nm compared to **5**, nearly twice as much as is caused by a change of Θ from 60 to 45° (from a C_4- to a C_3-bridged biphenyl [34]). Homoconjugation with the two bridges can be expected to contribute to the large bathochromic shifts. The intensities of the CD bands may again be related to couplings between the bridge and the biphenyl transitions. UV Spectra of simple sulfides in solution show a very weak absorption band at *ca.* 235 nm (S-1) and stronger bands at *ca.* 210 (S-2) and 200 nm (S-3) (oscillator strength 0.016 and 0.060, resp.) [38]. Theoretical studies of the three lowest singlet-singlet transitions in Me_2S predict that S-2 is polarized perpendicular to the C–S–C plane, while it was not possible to decide the polarization of S-3 [39][40]. It follows from *Eqn. 2* that the interaction between transitions 2 and S-2 should be weak due to the large difference in transition energies. Transitions 3 and S-2 are orthogonal and should give no couplet contribution. The dihedral angle between transitions 4 and S-2 is –64°, and a resulting negative couplet centered at *ca.* 210 nm may explain the low positive intensity of band 4 and the low negative intensity of band 6. We have at present no explanation for the low negative intensity of band 3.

As for (–)-**2** and (–)-**3**, we can conclude that the differences between the CD spectra of (–)-**4** and (*S*)-**5** are small and may be ascribed to effects of substituents and interactions with the bridge chromophores. Therefore, we confidently assign the absolute configuration of (–)-**4** as (*S*).

The UV and CD spectra of compounds **2**–**4** show no individual bands, which can be ascribed to transitions in the bridge chromophores. In the case of the UV spectra, this may be ascribed to the weakness of these transitions and, in case of the CD spectra, to overlapping of the bridge and biphenyl bands. Band 4 in the spectrum of **2** is unusually broad and may conceal a positive branch of a couplet generated mainly by interaction between SO-2 and a biphenyl transition.

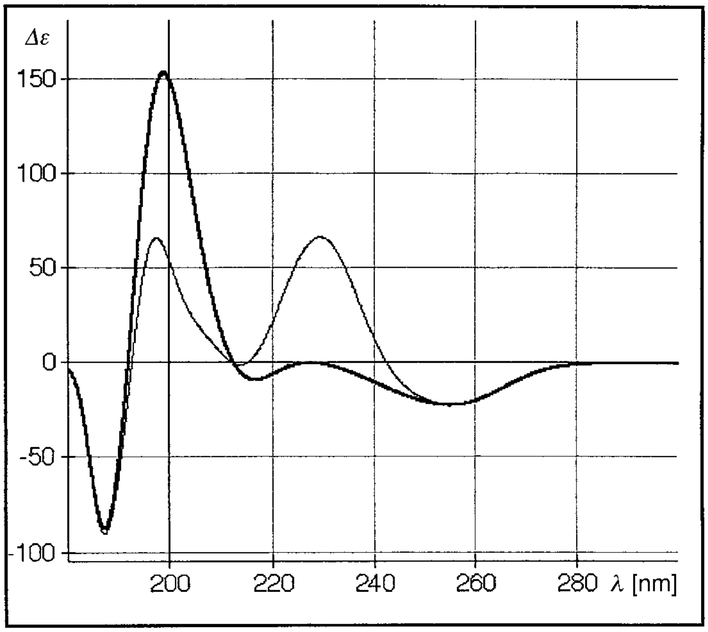

Fig. 10. *Theoretical CD spectra of (*S*)*-**2**. First calculation: —; one band displaced: —.

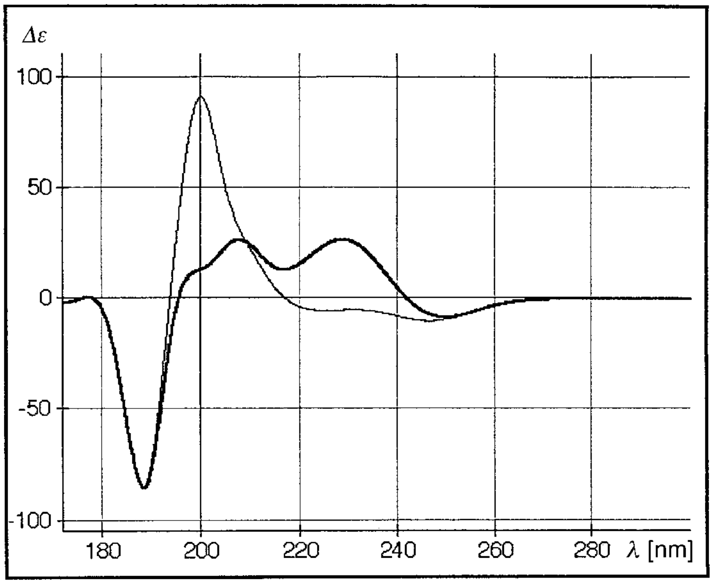

Fig. 11. *Theoretical CD spectra of (*S*)*-**3**. First calculation: —; one band displaced: —.

As mentioned earlier, CNDO/S calculations reproduce the CD spectrum of **5** in a qualitatively satisfactory manner (*Fig. 4*). The sequence of signs of the bands is correct, and the predicted positions and intensities of the bands are reasonable. Similar calculations on (*S*)-**4** also gave satisfactory results (*Fig. 7*). However, the calculations fail to reproduce the unusually strong band 1. Two very weak transitions with opposite signs are predicted at 287 nm.

The calculated spectra of (*S*)-**2** (*Fig. 10*) and (*S*)-**3** (*Fig. 11*) are less satisfactory. Both spectra display a rather strong positive band near 230 nm (*Table 6*, numbers in boldface), which lacks counterparts in the experimental spectra. Inspection of the calculations reveals that it is due to a *y*-polarized transition, while a strong transition corresponding to transition 5 with the same polarization in the range of 195–210 nm is missing. A reasonable interpretation is that the red-shift of this transition by the conjugation with CH_2SOCH_2 and $CH_2SO_2CH_2$, respectively, is predicted to be unrealistically large. If this band is moved from *ca.* 230 nm to 200 nm, much better agreement with the experimental spectra is obtained (see *Figs. 10* and *11*).

The predicted transition energies (*Table 6*) are often in good agreement with the experimental ones, with the transitions 5 discussed above as the most notable exceptions.

Summing up, the absolute configurations of compounds **2**, **3**, and **4** can confidently be assigned on the basis of comparisons of their CD spectra with that of **5**. The differences are far too small to be compatible with a reversal of configuration. They can, to a large extent, be explained by interactions between the biphenyl and the bridging chromophores. Calculations of CD spectra by the CNDO/S method support these assignments, unconditionally for **4**, and, after a reasonable correction, also for **2** and **3**.

It is worth noting that the (*S*)-enantiomers are eluted first from the triacetylcellulose column for all three compounds. For a series of C_4-bridged biphenyls, the (*R*)-enantiomers were eluted first when the bridge lacked substituents or had only equatorial substituents. The reverse was found for compounds with axial substituents in the bridge [41].

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