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# Determination of the absolute configurations of isotopically chiral molecules using vibrational circular dichroism (VCD) spectroscopy: the isotopically chiral sulfoxide, perdeuteriophenyl-phenyl-sulfoxide

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**Abstract**—The (+) and (−) enantiomers of the isotopically chiral sulfoxide, perdeuteriophenyl-phenyl-sulfoxide, **1**, have been synthesized by the reaction of the diastereomers of *O*-menthyl benzenesulfinate with $C_6D_5MgBr$. Their absolute configurations have been determined by comparison of the vibrational circular dichroism (VCD) spectra of (*R*)-**1** and (*S*)-**1**, predicted using ab initio DFT, to the experimental VCD spectrum of **1**. The absolute configuration of **1** is shown to be (*S*)(+)/(*R*)(−). This is the first application of VCD to the determination of the absolute configuration of an isotopically chiral sulfoxide.


## 1. Introduction

Over the last three decades enantiopure sulfoxides have been widely recognized as valuable optically active starting materials and as important chiral auxiliaries in organic synthesis that are able to bring about many asymmetric transformations. Their use as chiral synthons has now become well-established and is developing rapidly into an exciting area.[1] This results from at least two reasons. First, a variety of optically active sulfoxides are relatively easily available via the Andersen route[1a,2,3] or by asymmetric oxidation of the parent, prochiral sulfides.[2] Second, the chiral sulfinyl group is able to exert high asymmetric induction in a number of reactions, due to the steric and stereoelectronic differences that exist between the substituents bonded to the stereogenic sulfinyl sulfur atom. A lone electron pair, an oxygen, and two carbon-derived substituents are able to differentiate effectively the diastereotopic atoms or faces of a proximal reaction center, or even of a more remote prochiral reaction center. Additionally, the chiral sulfinyl residue, which induces chirality transfer, can be reduced in the resulting optically active molecules under very mild reaction conditions into an achiral sulfenyl group,[4] thus allowing efficient syntheses of enantiomeric structures, which in turn can be very easily converted into enantiomeric, sulfur-free end products. Moreover, the sulfinyl moiety is frequently found in bioactive natural products. Due to a wide range of biological activity (from flavor and aroma precursors to antimicrobial activity) chiral sulfoxides are often considered and tested as good candidates for synthetic drugs.[5] Considering the use of optically active sulfoxides as chiral auxiliaries in asymmetric synthesis and their bioactivity, it would be interesting to evaluate the efficiency and activity of derivatives, which are chiral by virtue of isotopic substitution (H–D or $^{12}C$–$^{13}C$, respectively). Such derivatives have already been prepared as optically active species by the reaction of the appropriate unlabeled optically active sulfinates with fully deuterated methylmagnesium iodide,[6] *n*-butyl-$d_9$-magnesium bromide,[7] and benzylmagnesium chloride prepared from benzyl-$^{13}C$ chloride.[8] Despite the extensive literature describing the use of optically active sulfoxides as models in mechanistic studies and as chiral auxiliaries in asymmetric synthesis and bioactive structures, a limited number of methods have been used to determine their absolute configurations. In particular, only a few examples of correlation between the electronic circular

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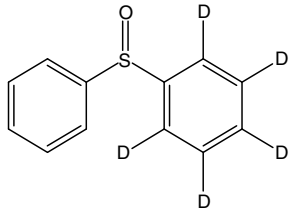
dichroism (ECD) and the structure of optically active sulfoxides have been reported.[9] These are based on an empirical rule formulated by Mislow et al. after examining the chiroptical properties of several alkyl aryl sulfoxides of known absolute configuration.[10] Recently, this empirical rule has found strong support from the non-empirical analysis of a series of ECD spectra of optically active alkyl aryl sulfoxides, using the coupled-oscillator model for non-degenerate transitions.[11] More recently, the first non-empirical correlation of absolute configuration and chiroptical properties of alkyl aryl *N*-phthalimidosulfoximines, based on the analysis of their exciton-split bichromophoric Cotton effects, has been reported.[12] The results of this correlation were applied simultaneously to determine the absolute configuration of the parent alkyl aryl sulfoxides due to the fact that *N*-phthalimidosulfoximines can be derived from sulfoxides via a reaction whose mechanism is believed to retain the configuration at the stereogenic sulfur atom.[13]

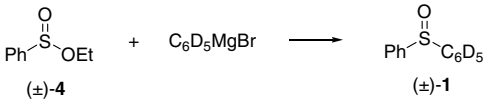
In the mid-1990s, a more reliable method for determining absolute configurations of chiral molecules was developed, in which ab initio density functional theory (DFT) calculations of vibrational circular dichroism (VCD) spectra are used to analyze experimental VCD spectra.[14] VCD has been used to analyze the stereochemistries of several chiral sulfoxides.[15] Herein, we report the application of VCD to the determination of the absolute configuration of the isotopically chiral sulfoxide, phenyl perdeuteriophenyl sulfoxide, **1**.



**1**

## 2. Results and discussion

Samples of racemic and optically active perdeuteriophenyl-phenyl-sulfoxide **1** were synthesized via the Andersen approach.[3] The dextro- and levorotatory enantiomers of **1** were prepared using the diastereomeric benzenesulfinates **2**, synthesized from (−)-(1*R*,2*S*,5*R*)- and (+)-(1*S*,2*R*,5*S*)-menthol, respectively, and benzenesulfinyl chloride using the procedure of Herbrandson and Dickerson[16] (modified by the use of $Et_3N$ instead of pyridine and by crystallization from petroleum ether instead of methanol), Scheme 1. The (*S*) and (*R*) absolute configurations of (−)-**2** and (+)-**2** at the sulfur atom were established by their conversion to optically active methyl phenyl sulfoxide **3**, of known absolute configuration[17] and enantiomeric excess,[18] by reaction with methylmagnesium iodide, which is assumed to cause full inversion of configuration at the sulfinyl sulfur atom,[1a,2a,10] Scheme 1. Then, the (−) and (+) enantiomers of the *O*-menthyl benzenesulfinates **2** were treated with perdeuteriophenyl-magnesium bromide giving the (+) and (−) isomers of perdeuteriophenyl-phenyl-sulfoxide **1**; assuming the inversion of configuration of the *S* atom, these isomers are expected to have the (*S*) and (*R*) configurations, respectively, Scheme 1. Simultaneously, racemic phenyl perdeuteriophenyl sulfoxide [(±)-**1**] was prepared using racemic *O*-ethyl benzenesulfinate **4** and phenyl-$d_5$-magnesium bromide (Eq. 1).

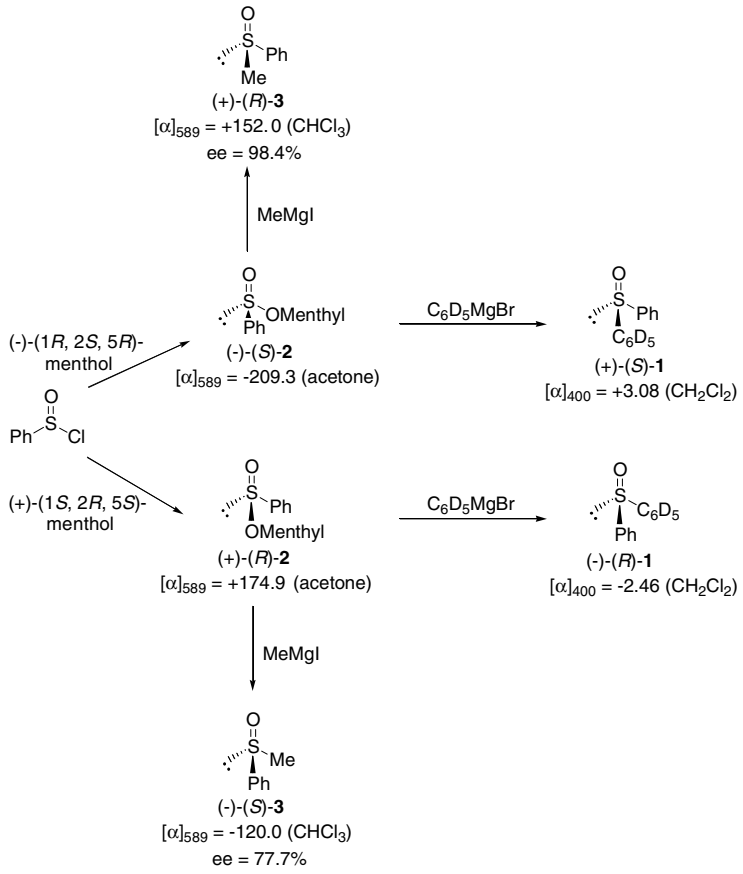


(±)-**4** (1)

The mid-IR IR and VCD spectra of (+)-**1** and (−)-**1** were measured using 0.1 M solutions in $CCl_4$. Measurements of the mid-IR IR spectrum of $CCl_4$ solutions of diphenyl-sulfoxide over the concentration range 0.01–0.4 M demonstrated that Beer's Law is obeyed up to 0.4 M, and, therefore, that aggregation of **1** does not occur at 0.1 M. The IR and VCD spectra of (+)-**1** in the frequency range 1150–1550 $cm^{-1}$ are shown in Figure 1. The two absorption bands at 1317 and 1445 $cm^{-1}$ exhibit large VCD of opposite signs.

The phenyl rings in **1** can rotate about the S–C bonds connecting them to the sulfoxide group. To establish the number of stable conformations of **1** that exist, a 2D potential energy surface (PES) scan with respect to the dihedral angles OSC1C2 and OSC3C4 was carried out using DFT, at the B3LYP/6-31G* level. Variation of the two dihedral angles from +60° to −60° led to the results shown in Figure 2. A single valley in the PES is present, demonstrating that over this range of dihedral angles, only one stable conformation exists. A 2D PES scan in which the two dihedral angles are varied from +180° to −180° found no additional, inequivalent, conformations. It is clear, therefore, that **1** is a conformationally-rigid molecule. To obtain the equilibrium geometry of **1**, the lowest-energy geometry in the 2D PES scan in Figure 2 was optimized. The values of the OSC1C2 and OSC3C4 dihedral angles of the optimized geometry are −8.8° and +8.8°, respectively. These values are in good agreement with the dihedral angles of the structure of diphenyl-sulfoxide determined using X-ray crystallography,[19] −11.7° and +11.4°, respectively.

As in previous work,[14,15a,c–f,20] the IR and VCD spectra of **1** have been predicted using DFT, with the functionals B3LYP and B3PW91 and the basis set TZ2P; use of the latter instead of 6-31G* reduces basis-set error in the predicted spectra. The B3LYP/TZ2P equilibrium geometry has OSC1C2 and OSC3C4 dihedral angles of −10.2° and +10.2°, respectively, closer to the X-ray values than those of the B3LYP/6-31G* geometry. The predicted IR spectrum of **1** and the VCD spectra of (*R*)-**1** and (*S*)-**1** are compared to the experimental spectra of (+)-**1** in Figures 3 and 4. Figure 4 shows that the predicted VCD spectra of (*S*)-**1** are qualitatively identical to the experimental VCD spectrum of (+)-**1**; the absolute configuration of (+)-**1** is clearly (*S*). The B3LYP/TZ2P and B3PW91/TZ2P spectra of (*S*)-**1** are similar, but not identical, especially for the VCD of the transitions of the normal modes 46–50. The B3LYP/TZ2P VCD spectrum of (*S*)-**1** is in better agreement with the experimental VCD spectrum of (+)-**1** than the B3PW91/TZ2P spectrum. Assignment of the IR and VCD spectra of **1** is, therefore, based on the B3LYP/TZ2P spectra. As




**Scheme 1.**

shown in Figures 3 and 4, the bands observed in the 1150–1550 $cm^{-1}$ range are due to the fundamental transitions of normal modes 44–52. The dominant VCD bands at 1317 and 1445 $cm^{-1}$ are assigned to modes 48 and 51, respectively. The predicted $\varepsilon$ and $\Delta\varepsilon$ values of modes 44–52 are in excellent quantitative agreement with the experimental values, further supporting the accuracy of the B3LYP/TZ2P spectra and the assignment of the absolute configuration of (+)-**1** as (*S*).

## 3. Conclusion

Comparison of the VCD spectra of (*R*)-**1** and (*S*)-**1**, predicted using DFT, to the experimental VCD spectrum of (+)-**1** proves unambiguously that the absolute configuration of **1** is (*S*)(+)/(*R*)(−). This configuration is the same as that deduced from the syntheses of (+)-**1** and (−)-**1** from (−)-**2** and (+)-**2** (Scheme 1), assuming inversion of the configuration of the *S* atom, proving that this mechanism is indeed correct.

The efficiency of VCD in assigning the absolute configuration of an isotopically chiral sulfoxide has been demonstrated. At the present time, the ECD and ORD spectra of isotopically chiral sulfoxides cannot be reliably analyzed. VCD is, therefore, the optimum chiroptical technique for determining the absolute configurations of isotopically chiral sulfoxides.

## 4. Experimental

### 4.1. General

$^1$H NMR spectra were recorded at 200 MHz on a Brucker spectrometer. All optical rotation measurements were done on a Perkin–Elmer 241 MC polarimeter. Mass spectra were obtained by direct probe using a Finigan MAT 20 mass spectrometer. Silica gel (230–400 mesh) chromatography was used to purify the prepared sulfoxides. Analytical TLC was performed on Merck aluminum plates coated with silica gel. A UV lamp (254 nm) was used to locate compounds containing aromatic rings. All air and moisture sensitive reactions were carried out under $N_2$. Bromobenzene-$d_5$ (99.5 atom % D) was purchased from Armar AG, Dottingen (Switzerland). Separate procedures for the preparation of (+)-**1** ($[\alpha]_{400} = +3.08$, *c* 2.11, $CH_2Cl_2$, ee = 98.4%), (−)-**1** ($[\alpha]_{400} = -2.46$, *c* 1.42, $CH_2Cl_2$, ee = 77.7%) and racemic **1** are given below. The ee values of (+)-**1** and (−)-**1** were assumed to be the same as those of the samples of (−)-**2** and (+)-**2** from which they were obtained, derived from the known ee's of (+)-**3** and (−)-**3** obtained by Grignard reaction of (−)-**2** and (+)-**2** with MeMgI,

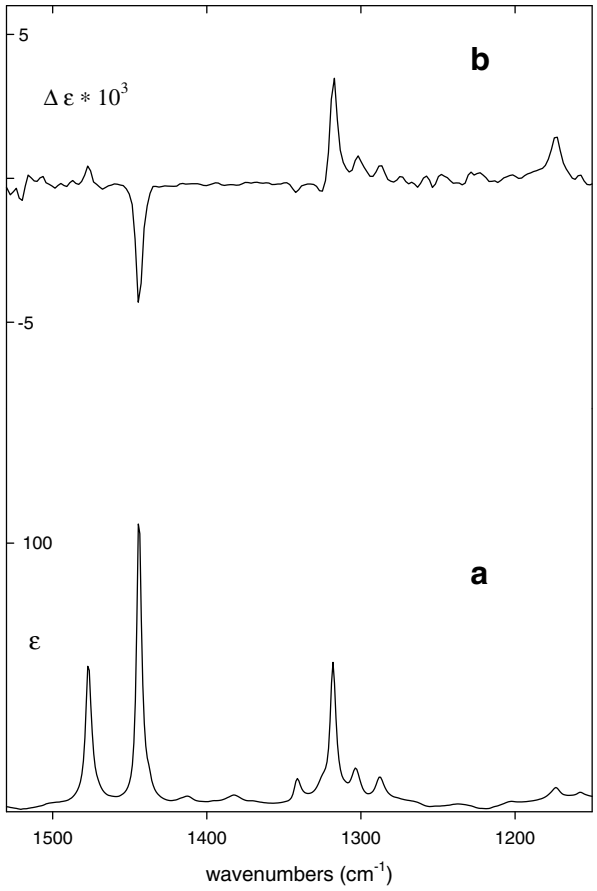



**Figure 1.** (a) The IR spectrum of a 0.10 M $CCl_4$ solution of (+)-**1**. Pathlength 597 μ. (b) The VCD 'half-difference' spectrum of (+)-**1**, 1/2 [$\Delta\varepsilon(+) - \Delta\varepsilon(-)$], obtained from the VCD spectra of 0.10 M $CCl_4$ solutions of (+)-**1** and (−)-**1**. Given the 27% higher ee of (+)-**1**, compared to (−)-**1**, the VCD of (−)-**1** was multiplied by 1.27.

which is assumed to occur with full inversion of configuration of the sulfinyl *S* atom. Unfortunately, all attempts to support our ee determinations by HPLC on chiral columns have so far been unsuccessful.

### 4.2. The dextrorotatory enantiomer (+)-1

**4.2.1. *O*-(1*R*,2*S*,5*R*)-(−)-Menthyl-(*S*)-benzenesulfinate (−)-(*S*)-2.** A solution of (1*R*,2*S*,5*R*)-(−) menthol (22.4 g, 143 mmol) and triethylamine (16.2 g, 160 mmol) in $Et_2O$ (100 mL) was added dropwise with vigorous stirring to a solution of benzenesulfinyl chloride (23.0 g, 143 mmol) in $Et_2O$ (150 mL) at −70 °C. After the reaction mixture was stirred for 6 h at −70 °C and a few hours at room temperature, the solution was diluted with diethyl ether (100 mL) and quenched with water. The organic phase was separated and washed with 5% $H_2SO_4$ solution, 5% $K_2CO_3$ solution and water and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude sulfinate (38 g) with $[\alpha]_D = -127.8$ (*c* 2.01, acetone) was purified by crystallization from petroleum ether at −18 °C giving the levorotatory diastereomer (5.3 g) with $[\alpha]_{589} = -209.3$ (*c* 1.45, acetone), mp 42–44 °C [lit.: 49–51 °C; $[\alpha]_D = -205.5$ (*c* 2.0, acetone)[15a] and 37–40 °C and $[\alpha]_D = -195.5$ (*c* 2.0, acetone)[15b]]; $^1$H NMR (200 MHz, $CDCl_3$) $\delta = 0.71$ (d, 3H, $^2J_{H-H} = 6.9$ Hz, $CH_3$); 0.86 [d, 3H, $^2J_{H-H} = 6.9$ Hz, $(CH_3)_2CH$]; 0.96 [d, 3H, $^2J_{H-H} = 6.9$ Hz, $(CH_3)_2CH$]; 1.00–2.30 [m, 8H, *cyclohexane ring protons*]; 4.13 and 4.15 [2t, 1H, $^2J_{H-H} = 6.9$ Hz, (–C*H*–OH)]; 7.45–7.52 (m, 3H-aromatic), 7.67–7.85 (m, 2H-aromatic); $^{13}$C NMR (50.34 MHz, $CDCl_3$) $\delta = 124.36$ (t, $J_{13C-D} = 25.2$ Hz); 124.74 (s); 128.77 (t, $J_{13C-D} = 24.6$ Hz); 15.44; 20.82; 22.03; 23.14; 25.22; 31.72; 33.99; 42.94; 47.86; 80.36; 125.02; 128.94; 145.39 (s); 131.82.

Other crops of the levorotatory diastereomer with $[\alpha]_{589}$ from −199 to −209 (*c* 1.3, acetone) were obtained after repeated crystallization.

**4.2.2. (+)-Phenyl perdeuteriophenyl sulfoxide (+)-1.** To a solution of perdeuteriophenyl-magnesium bromide in diethyl ether (15 mL) prepared from bromobenzene-$d_5$ [0.942 g, 6 mmol and magnesium (0.144 g, 6 mmol)] was added dropwise at room temperature a solution of the levorotatory sulfinate obtained above (1.184 g, 4 mmol) in diethyl ether (10 mL). After the reaction mixture was stirred for 3 h at room temperature, it was quenched with 5% $H_2SO_4$ solution and diluted with water (200 mL). The organic solution was separated from the aqueous phase, and the aqueous phase was extracted with methylene chloride (3 × 50 mL). The organic extracts were dried over $MgSO_4$. Evaporation of the solvent gave the crude phenyl perdeuteriophenyl sulfoxide (1.21 g), which was purified by column chromatography on silica gel (30 g). The column was washed subsequently with petroleum ether (24 × 10 mL), petroleum ether/diethyl ether [7:3 v/v (64 × 10 mL)], and methylene chloride (150 mL). Evaporation of petroleum ether/diethyl ether (7:3) fractions 57–64 and the methylene chloride solution gave the pure sulfoxide (0.234 g) with $[\alpha]_{400} = +3.08$ (*c* 2.11, $CH_2Cl_2$), mp 67–68 °C, $^1$H NMR (200 MHz, $CDCl_3$) $\delta = 7.38$–7.52 (m, $3H_{aromatic}$), 7.59–7.68 (m, $2H_{aromatic}$); $^{13}$C NMR (50.34 MHz, $CDCl_3$) $\delta = 124.36$ (t, $J_{13C-D} = 25.2$ Hz); 124.74 (s); 128.77 (t, $J_{13C-D} = 24.6$ Hz); 129.28(s); 130.99 (t, $J_{13C-D} = 24.7$ Hz); 132.33 (s); 145.39 (s);145.57 (s); MS (EI) ($m/z$) = 207.1; HRMS $m/z$: calcd for $C_{12}H_5D_5OS$, 207.07660; found, 207.07691.

### 4.3. The levorotatory enantiomer (−)-1

**4.3.1. *O*-(1*S*,2*R*,5*S*)-(+)-Menthyl-(*R*)-benzenesulfinate (+)-(*R*)-2.** A solution of (1*S*,2*R*,5*S*)-(+) menthol (7.8 g, 50 mmol) and triethylamine (5.6 g, 55 mmol) in $Et_2O$ (30 mL) was added dropwise with vigorous stirring to a solution of benzenesulfinyl chloride (8.0 g, 50 mmol) in $Et_2O$ (100 mL) at −70 °C. After the reaction mixture was stirred for 6 h at −70 °C and a few hours at room temperature, the solution was diluted with diethyl ether (100 mL) and quenched with water. The organic phase was separated and washed with 5% $H_2SO_4$ solution, 5% $K_2CO_3$ solution and water and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude sulfinate (13.73 g) with $[\alpha]_D = +94.6$ (*c* 1.4, acetone) was purified by crystallization from petroleum ether at −18 °C giving the dextrorotatory diastereomer (2.4 g) with $[\alpha]_{589} = +174.9$ (*c* 1.06, acetone), mp 39–41 °C. The spectral and

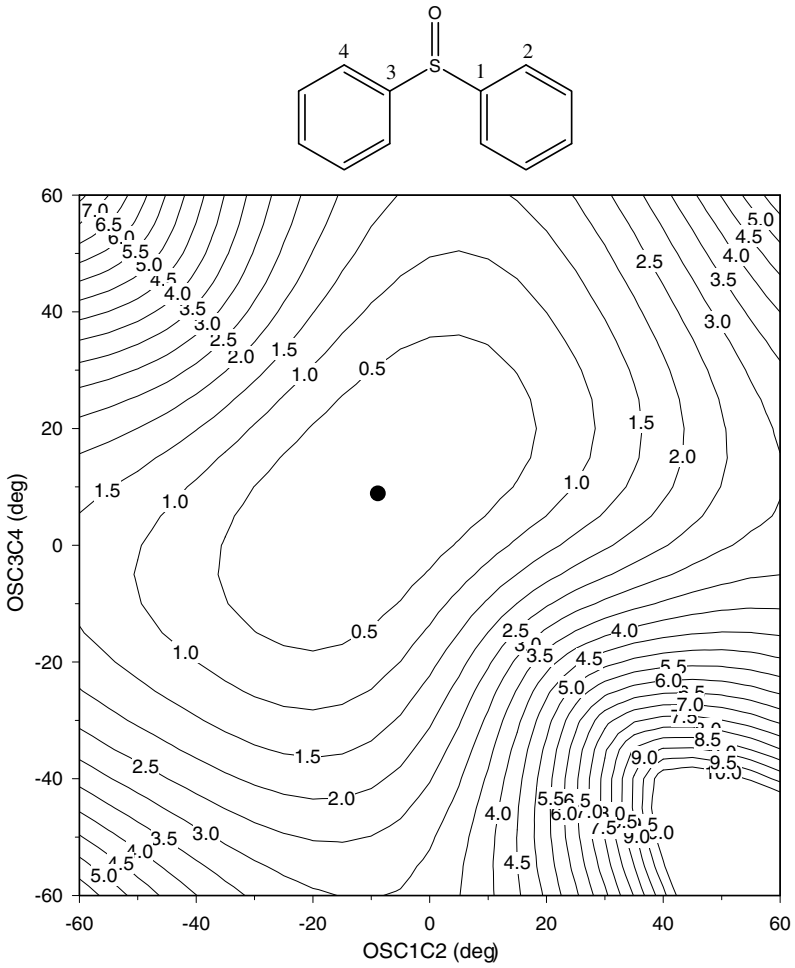



**Figure 2.** The B3LYP/6-31G* PES of diphenyl-sulfoxide, as a function of the dihedral angles OSC1C2 and OSC3C4. The two dihedral angles were varied in 5° steps over a range from −60° to +60°. Contours are shown at 0.5 kcal/mol intervals. ● is the B3LYP/6-31G* optimized geometry.

analytical data were in full agreement with those presented above for the levorotatory diastereomer.

Other crops of the dextrorotatory diastereomer with $[\alpha]_{589}$ close to +179 (*c* 1.1, acetone) were obtained after repeated crystallization.

**4.3.2. (−)-Phenyl perdeuteriophenyl sulfoxide (−)-1.** To a solution of perdeuteriophenyl-magnesium bromide in diethyl ether (15 mL) prepared from bromobenzene-$d_5$ [0.942 g, 6 mmol and magnesium (0.144 g, 6 mmol)] was added dropwise at room temperature a solution of the above obtained dextrorotatory sulfinate (1.184 g, 4 mmol) in diethyl ether (10 mL). After the reaction mixture was stirred for 3 h at room temperature, it was quenched with 5% $H_2SO_4$ solution and diluted with water (200 mL). The organic solution was separated from the aqueous phase, and the aqueous phase was extracted with methylene chloride (3 × 50 mL). The organic extracts were dried over $MgSO_4$. Evaporation of the solvent gave the crude phenyl perdeuteriophenyl sulfoxide (1.21 g), which was purified by column chromatography on silica gel (30 g). The column was washed subsequently with petroleum ether (250 mL), petroleum ether/diethyl ether 7:3 (30 × 10 mL), and methylene chloride (30 × 10 mL). Evaporation of the methylene chloride fractions from 6 to 30 gave the pure sulfoxide (0.263 g) with $[\alpha]_{400} = -2.46$ (*c* 1.42, $CH_2Cl_2$), mp 66–68 °C. The spectral and analytical data were in full agreement with those presented above for the dextrorotatory enantiomer.

### 4.4. (±)-Phenyl perdeuteriophenyl sulfoxide (±)-(1)

To a solution of perdeuteriophenyl-magnesium bromide in diethyl ether (15 mL) prepared from bromobenzene-$d_5$ [0.942 g, 6 mmol and magnesium (0.144 g, 6 mmol)] was added dropwise at room temperature a solution of *O*-ethyl benzenesulfinate (0.85 g, 5 mmol) in diethyl ether (10 mL). After the reaction mixture was stirred for 3 h at room temperature, it was quenched with 5% $H_2SO_4$ solution and diluted with water (200 mL). The organic solution was separated from the aqueous phase, and the aqueous phase was extracted with methylene chloride (3 × 50 mL). The organic extracts were dried over $MgSO_4$. Evaporation of the solvent gave the crude phenyl perdeuteriophenyl sulfoxide (0.751 g), which was purified by column chromatography on silica gel (30 g). The column was washed subsequently with petroleum ether (50 mL), petroleum

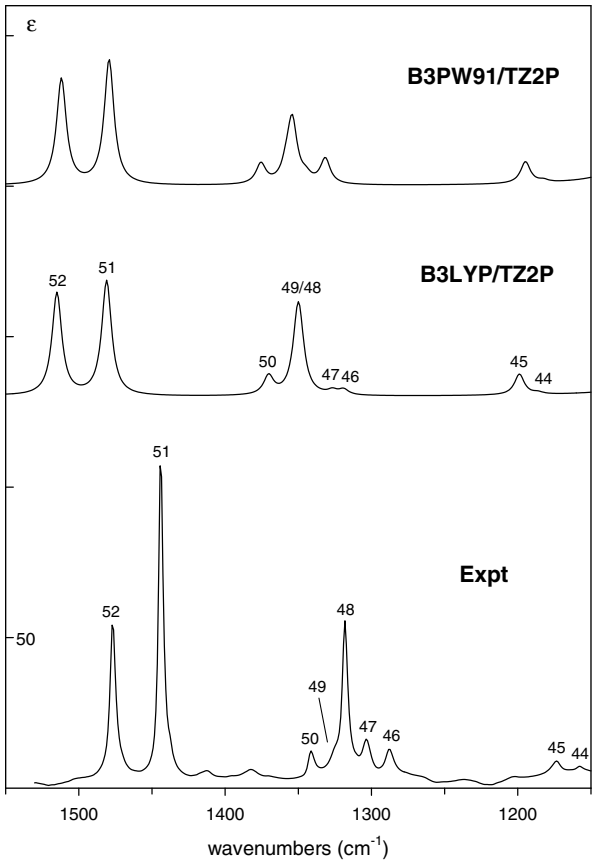



**Figure 3.** Comparison of the B3LYP/TZ2P and B3PW91/TZ2P IR spectra of **1** to the experimental IR spectrum. The assignment of the experimental spectrum is based on the B3LYP/TZ2P spectrum. The calculated IR spectra have Lorentzian bandshapes ($\gamma = 4.0\ cm^{-1}$).

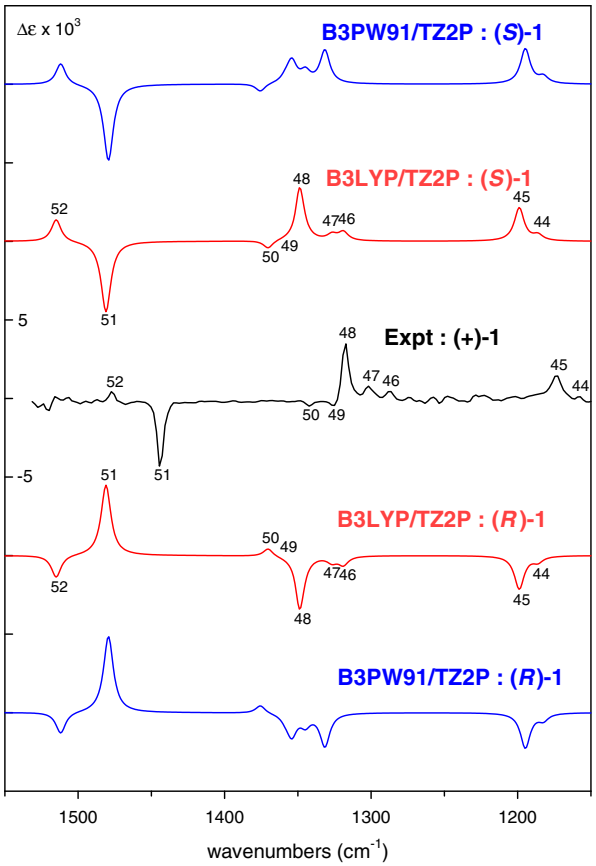



**Figure 4.** Comparison of the B3LYP/TZ2P and B3PW91/TZ2P VCD spectra of (*R*)-**1** and (*S*)-**1** to the experimental VCD spectrum of (+)-**1**. The assignment of the experimental spectrum is based on the B3LYP/TZ2P spectrum of (*S*)-**1**. The calculated VCD spectra have Lorentzian bandshapes ($\gamma = 4.0\ cm^{-1}$).

ether/diethyl ether 7:3 (50 mL), and methylene chloride (100 mL). Evaporation of the methylene chloride fractions gave the pure sulfoxide (0.363 g), mp 65–66 °C. The spectral and analytical data were in full agreement with those presented above for the dextrorotatory enantiomer.

### 4.5. IR and VCD spectra

The IR and VCD spectra of (+)-**1**, (−)-**1** and (±)-**1** were measured using $CCl_4$ solutions of 0.1 M concentration, Thermo-Nicolet Nexus 670 IR and Bomem/BioTools VCD instruments. Scan times and resolution of the VCD spectra were 1 h and 4 $cm^{-1}$, respectively. The mid-IR IR spectra of (+)-**1**, (−)-**1** and (±)-**1** were identical, demonstrating that the samples were of equal chemical purity; contributions to the IR and VCD spectra of impurities are, therefore, unlikely. The VCD spectra of (±)-**1** provided the baseline for the VCD spectra of (+)-**1** and (−)-**1**, minimizing the contributions of artifacts to the spectra.

The DFT harmonic frequencies, dipole strengths and rotational strengths of (*R*)-**1** and (*S*)-**1** were calculated using GAUSSIAN 03.[21] IR and VCD spectra were obtained thence using Lorentzian bandshapes[22] with $\gamma = 4.0\ cm^{-1}$.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