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Absolute Configuration, Predominant Conformations, and Vibrational Circular Dichroism Spectra of Enantiomers of *n*-Butyl *tert*-Butyl Sulfoxide

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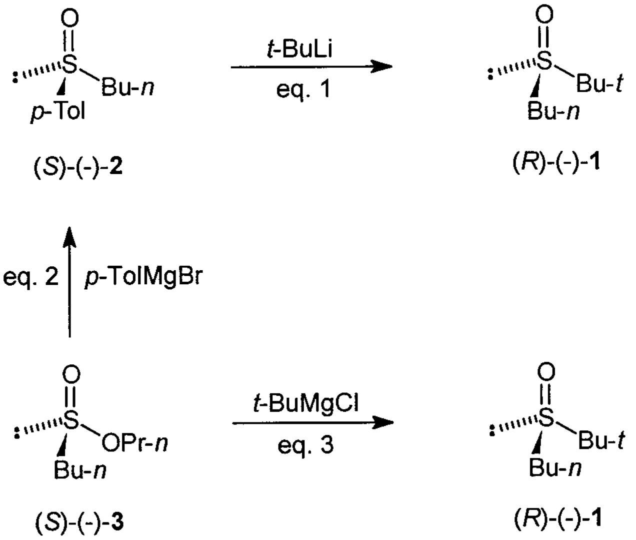
Alkylation of the α-carbanion of (*R*)-(−)-*tert*-butyl methyl sulfoxide (**4**) with *n*-propyl bromide afforded (+)-*n*-butyl *tert*-butyl sulfoxide (**1**) to which the absolute configuration (*R*) was ascribed. This assignment was confirmed by X-ray analysis of the complex **6** obtained from the enantiomerically pure sulfoxide (−)-**1** and mercury chloride. Vibrational absorption and circular dichroism spectra of (+)-**1** were measured in $CDCl_3$ solution in the 2000−900 cm^{-1} region and compared with the ab initio predictions of absorption and VCD spectra obtained with density functional theory using the B3LYP/6-31G* basis set for different conformers of (*R*)-**1**. This comparison indicated also that (+)-**1** is of the (*R*)-configuration.

Introduction

Chiral sulfoxides belong to the class of chiral organosulfur compounds which are often used in stereoselective and asymmetric synthesis.[1,2] Their application as chiral auxiliaries has now become a well-established and reliable strategy, especially for asymmetric C−C bond formation. The commonly used method for the preparation of enantiomerically pure sulfoxides is based on the conversion of the appropriately constructed diastereomeric or enantiomeric sulfinic acid derivatives (sulfinates, thiosulfinates, sulfinamides) or even the selected group of enantiomeric sulfoxides into sulfoxides with various types of organometallic reagents.[1] The absolute configuration of the sulfoxides obtained by this methodology was assigned by assuming inversion of configuration at the sulfinyl sulfur atom in the nucleophilic substitution step.

On the basis of this assumption, Johnson and coworkers[3] as early as 1973 ascribed the absolute configuration (*S*) to the dextrorotatory enantiomer of *n*-butyl *tert*-butyl sulfoxide (**1**) formed in the reaction between (*R*)-(+)-*n*-butyl *p*-tolyl sulfoxide (**2**) and -*tert*-butyllithium (eq 1 in Scheme 1). More recently, taking advantage of this assignment, our group from Łódź[4] constructed the stereochemical cycle (Scheme 1) which indicated that the reaction of (*S*)-(−)-*O*-*n*-propyl *n*-butanesulfinate (**3**) with *tert*-butylmagnesium chloride leading to (−)-**1** (eq 3 in Scheme 1) was occurring with retention of configuration at sulfur.

Scheme 1



At the same time, the enantiomeric sulfoxides (+)-**1** and (−)-**1** were prepared by Kagan[5] using his chiral sulfite methodology and independently by Evans[6] from

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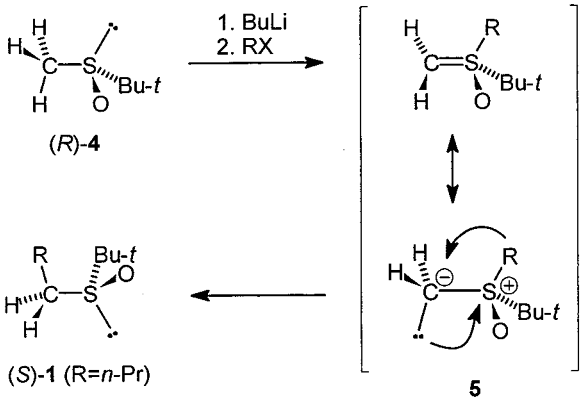
10.1021/jo0011179 CCC: $20.00

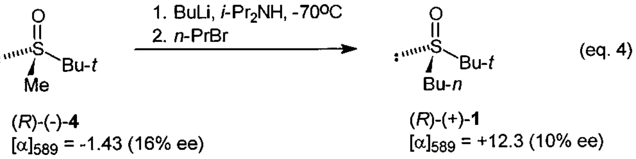
Scheme 2



chiral *N*-sulfinyloxazolidinones. However, their configurational assignments were opposite to those reported by Johnson, i.e., (*R*) for (+)-**1** and (*S*) for (−)-**1**. In light of this discrepancy, an independent verification of the absolute configuration of **1** would therefore be desirable. In this paper we wish to report unequivocal proof of the absolute configuration of the enantiomeric sulfoxides **1** as well as their vibrational circular dichroism spectra which in combination with calculations, may be used as an useful method for the configurational assignments of this class of chiral sulfur compounds.

Results and Discussion

Chemical Correlation. In the first step, we decided to correlate the absolute configuration of optically active sulfoxide **1** with that of (*R*)-(−)-*tert*-butyl methyl sulfoxide (**4**) whose absolute configuration has recently been established by us by a combined chemical-crystallographic method.[7] Thus, the α-carbanion generated from the optically active sulfoxide **4**, enriched in the levorotatory enantiomer, was treated with *n*-propyl bromide to give (+)-*n*-butyl *tert*-butyl sulfoxide (**1**) (eq 4).



By making the very reasonable assumption that alkylation of the anion derived from (−)-**4** occurs directly at the α-carbon atom and that there is no bond breaking around sulfur, it is possible to assign the absolute configuration (*R*) to the sulfoxide (+)-**1**. This assignment is in accord with the assignments reported by Kagan and Evans.

However, one can envisage a mechanism that results in the α-alkylation accompanied by inversion at sulfur. Alkylation of the sulfoxide **4** anion by this mechanism should primarily occur at sulfur to give the sulfoxonium ylide **5** which can undergo rearrangement to the final sulfoxide **1** with inversion at sulfur as depicted in Scheme 2.

Although the above mechanistic proposal is very sophisticated, it is interesting to point out that inversion at sulfur was observed in α-halogenation of some chiral sulfoxides and explained in a similar way.[8]

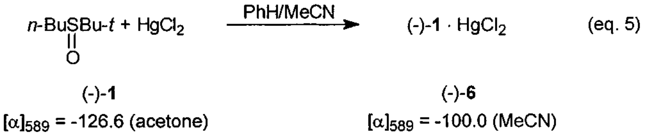
Table 1. Steric Course of the Reaction of (−)- or (+)-*n*-Butyl *p*-Tolyl Sulfoxide (2)

	sulfoxide **2**			sulfoxide **1**		
no. of expts	$[\alpha]_{589}$	ee (%)	abs confign	$[\alpha]_{589}$	ee (%)	abs confign
1	−44.6	21.2	*S*	+16.7	12.9	*R*
2	−44.6	21.2	*S*	+2.5	1.9	*R*
3	+209	100	*R*	−129.4	100	*S*
4	+209	100	*R*	+29.5	22.8	*R*
5	+209	100	*R*	−123.6	95.8	*S*
6	+210	100	*R*	−11.6	86.5	*S*
7	+203	96.7	*R*	−126.6	98.1	*S*
8	+192	91.4	*R*	−37.5	29.1	*S*
9	+192	91.4	*R*	−15.0	11.6	*S*
10	−177	84.3	*S*	−47.8	37.0	*S*

The result of our chemical correlation prompted us to repeat the synthesis of the optically active sulfoxide **1** according to the Johnson procedure. Unexpectedly, it turned out that the stereochemical outcome of this reaction (eq 1, Scheme 1) varied from experiment to experiment (Table 1). The only difference in our experiments was the use of *tert*-butyllithium from different sources having different concentrations and the time of aging and contaminated with different amounts of inorganic salts.[9]

An inspection of the results collected in Table 1 clearly indicates that only in two cases (experiment nos. 4 and 10) could we reproduce the result described by Johnson. However, the stereoselectivity of these two reactions was much lower. In all other experiments the sulfoxide **1** was obtained from **2** with the opposite rotation sign, i.e., with inversion of configuration provided that the configurational assignments to the enantiomeric sulfoxides **1** by chemical correlation discussed above as well as by Kagan and Evans are correct.

Crystal and Molecular Structure of the Complex of (−)-1 with Mercury Chloride. In view of some doubts concerning the correctness of the configurational assignments to enantiomeric **1** by chemical correlation, we decided to solve this problem by the method which is unquestionable, i.e., by X-ray analysis. Unfortunately, the enantiomeric sulfoxides **1** are liquids. However, knowing that mercury chloride is able to form solid complexes with liquid sulfoxides,[10] we were able to obtain the crystalline complex **6** from the enantiomerically pure sulfoxide (−)-**1** and mercury chloride.



$$n\text{-BuS(=O)Bu-}t + HgCl_2 \xrightarrow{PhH/MeCN} (-)\text{-}\mathbf{1}\cdot HgCl_2$$

The X-ray crystal structure determination carried out on a single crystal of this complex by anomalous dispersion revealed unequivocally that the absolute configuration at the stereogenic sulfur atom in (−)-**1** is (*S*) as it is

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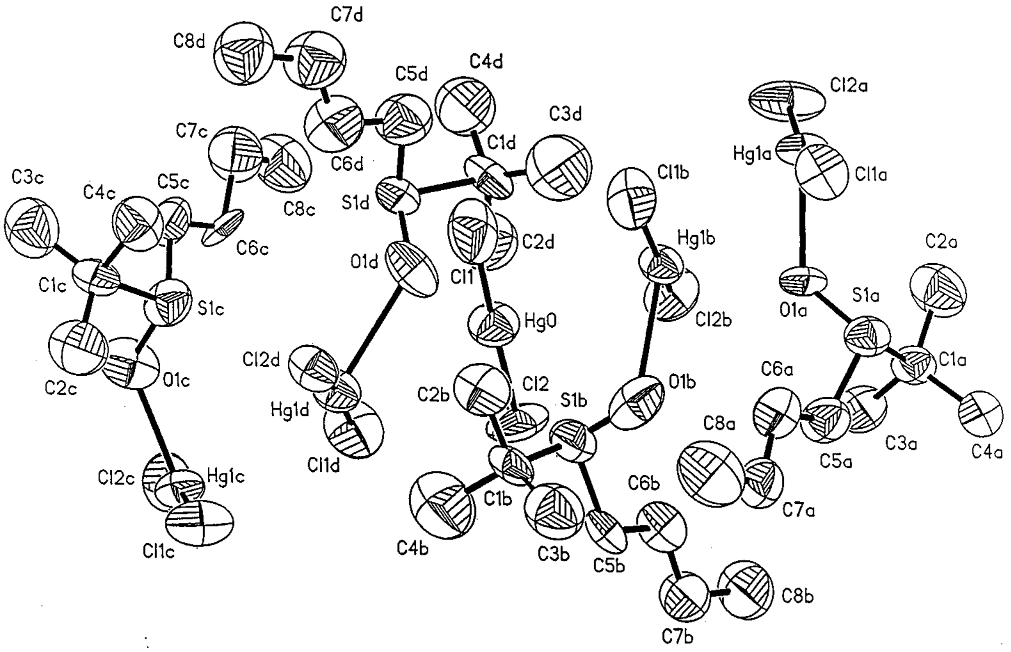

Figure 1. Thermal ellipsoidal plot of the complex of the levorotatory enantiomer of *n*-butyl *tert*-butyl sulfoxide **1** with mercury chloride with atom numbering scheme.

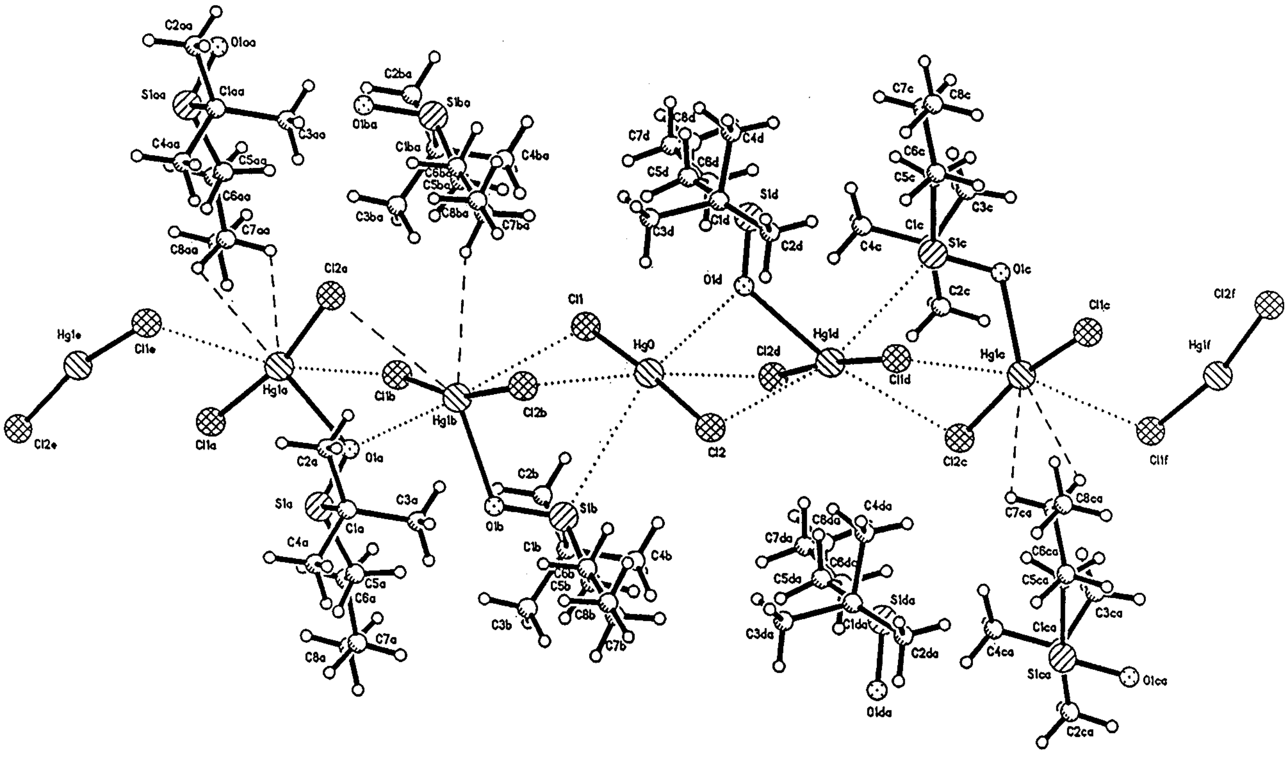

Figure 2. Unit cell and coordination bonding system.

clearly seen from Figure 1 which shows the thermal ellipsoidal plot of the complex with the atom numbering scheme.

The unit cell of **6** consists of four molecules of the sulfoxide (−)-**1** and five molecules of mercury chloride (see Figure 2). Four molecules of the latter are connected with four molecules of (−)-**1** via the mercury−oxygen bond (the Hg−O distances vary from 2.366 to 2.533 Å). The fifth one forms coordination bonds with the two chlorine atoms of the neighboring $HgCl_2$ molecules with the Hg···Cl distances of 3.173 and 3.216 Å as well as with sulfur and oxygen of the two closest molecules of (−)-**1** with the Hg···S and Hg···O distances of 3.700 and 2.811 Å, respectively. Interestingly, the mercury chloride molecules in the crystal lattice are held together via the Hg···Cl coordination bonds and form a linear chain situated between two sulfoxide layers.

Vibrational Circular Dichroism and Predominant Conformations of the Dextrorotatory Enantiomer of *n*-Butyl *tert*-Butyl Sulfoxide 1. The combination of experimental and ab initio absorption and vibrational circular dichroism (VCD) spectra has been used in recent years for determining the absolute configuration and predominant conformations of chiral molecules in the solution phase.[11−13] Successful determinations of both the absolute configurations and predominant conformations of 1,2,2,2-tetrafluoroethyl methyl ether,[11a] desflurane,[11b] epichlorohydrin,[11d] 3-butyn-2-ol,[11e] Troger's base,[13a] phenyloxirane,[13b] *tert*-butyl phenyl phosphine oxide,[13c] and *tert*-butyl methyl sulfoxide[13d] in solution phase are some recent examples that reflect the reliability of VCD method. The utility of VCD is facilitated by two advances: (a) improvements in VCD instrumentation have made it possible to obtain the VCD spectra with enhanced signal-to-noise ratio; (b) ab initio applications using density functional theory (DFT)[14] have become state-of-the-art in recent years. The DFT theory, which provides vibrational frequencies and intensities that are comparable to the post-SCF calculations employing electron correlation, has also been extended to the VCD intensity calculations[15] and implemented in standard software.[16] These developments make it possible to use VCD for reliable determination of the absolute configuration and predominant conformations in the solution phase.

Chiral sulfoxides, which contain the lone electron pair as a so-called phantom ligand, have not been investigated before using VCD. Also the quantum mechanical predictions of vibrational properties of *n*-butyl *tert*-butyl sulfoxide (**1**) have not been reported. Therefore, we have measured the VCD of the sulfoxide (+)-**1** and undertaken the state-of-the-art ab initio theoretical VCD investigations using B3LYP/6-31G* basis set. These results are used for suggesting the absolute configuration and predominant conformations of (+)-**1**.

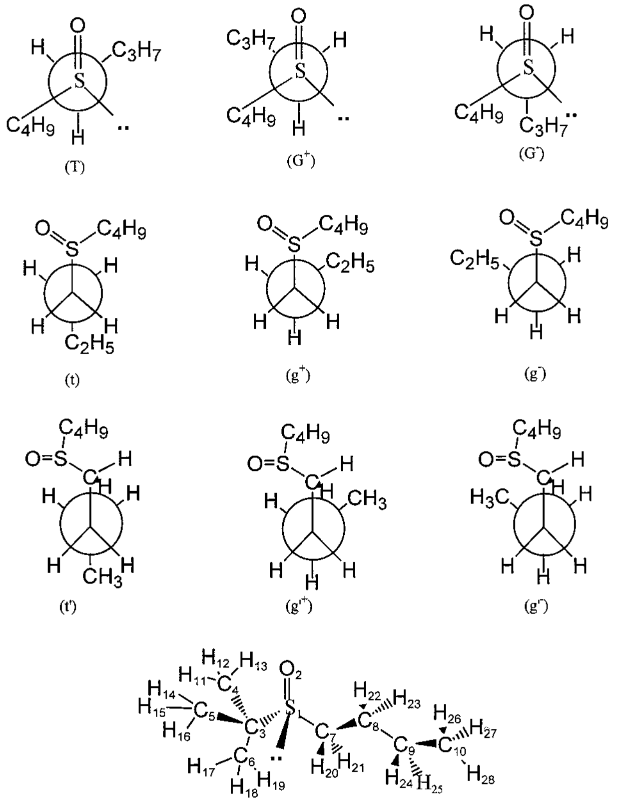

Figure 3. Different conformations of *n*-butyl *tert*-butyl sulfoxide **1**. T, G$^+$, and G$^-$ are conformations around the C−S−C−C dihedral segment; t, g$^+$, and g$^-$ are conformations around the S−C−C−C dihedral segment; t′, g′$^+$, and g′$^-$ are conformations around the C−C−C−C dihedral segment.

Using standard orientations around C−S−C−C, S−C−C−C, and C−C−C−C segments, one expects 27 possible conformations for *n*-butyl *tert*-butyl sulfoxide (**1**) (see Figure 3). The geometries were optimized with B3LYP/6-31G* basis set using the standard dihedral angles of 60°, 180°, or 300° for C−S−C−C, S−C−C−C, and C−C−C−C segments. Keeping the C−S−C−C segment in trans conformation, the geometries of the resulting nine conformations were optimized. When the C−S−C−C segment is in the gauche-plus or the gauche-minus conformation, the resulting energies are found to be higher in sample calculations [see the energies of (G$^+$, t, t′) and (G$^-$, t, g′$^+$) conformations in Table 2]. For this reason, the remaining possible conformations, while keeping the C−S−C−C segment in the G$^+$ or G$^-$ conformations, have not been pursued. The geometries of twelve conformations of (*R*)-*n*-butyl *tert*-butyl sulfoxide **1**, differing in the dihedral angles for C−S−C−C, S−C−C−C, and C−C−C−C segments, as listed in Table 2, have been optimized. The converged C−S−C−C, S−C−C−C, and C−C−C−C dihedral angles and optimized electronic energies are listed in Table 2. Ten conformations (see Figure 3) with the lowest energies have been chosen for vibrational spectral studies. Their Gibbs energies, and relative populations are listed in Table 2. Based on these relative populations, it can be concluded that the (T, t, t′) conformation is the most populated one for the isolated (*R*)-*n*-butyl *tert*-butyl sulfoxide (**1**).

All 10 lowest energy conformers were found to be minima on the potential energy surface (i.e., all vibrational frequencies are real) at the B3LYP/6-31G* level. The calculation for (T, t, t′) conformation was also carried out at a higher B3LYP/6-311G(2d,2p) level. A comparison of the results obtained in these two calculations shows that the calculated frequencies obtained using 6-311(2d,-2p) basis set are slightly lower than those obtained using 6-31G* basis set, but the predicted absorption and VCD spectra are nearly equal in the two calculations. Since the calculations with B3LYP/6-311G(2d,2p) are much more time-consuming. these calculations were not pursued further. The absorption and VCD intensities were

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Table 2. Conformations and Energies of (*R*)-*n*-Butyl *tert*-butyl Sulfoxide

		converged geometry[b]			energy[c]			
no.	label[a]	CSCC	SCCC	CCCC	electronic	Gibbs	ΔE[d]	pop.[e]
1	(T,t,t′)	172.0	−177.7	177.5	−789.074763	−788.863475	0	32.5
2	(T,g$^+$,t′)	176.6	71.5	179.0	−789.073982	−788.863058	0.262	20.9
3	(T,g$^-$,t′)	−179.3	−76.6	−179.5	−789.073256	−788.862462	0.636	11.1
4	(T,t,g′$^-$)	170.9	−174.7	−65.2	−789.073608	−788.862330	0.718	9.7
5	(T,t,g′$^+$)	173.0	−180.0	65.8	−789.073320	−788.862227	0.783	8.7
6	(T,g$^-$,g′$^-$)	−167.6	−61.9	−57.9	−789.072509	−788.862016	0.916	6.9
7	(T,g$^+$,g′$^+$)	167.0	66.6	62.8	−789.072730	−788.861782	1.062	5.4
8	(G$^-$,t,t′)	−105.0	−175.0	179.5	−789.071542	−788.861135	1.468	2.7
9	(G$^+$,t,t′)	97.9	163.0	179.7	−789.071739	−788.860727	1.724	1.8
10	(T,g$^+$,g′$^-$)	157.8	80.9	−68.1	−789.071101	−788.859380	2.570	0.4
11	(G$^-$,t,g′$^+$)	−105.0	178.0	65.1	−789.070363			
12	(T,g$^-$,g′$^+$)	−158.8	−76.1	78.6	−789.070091			

[a] T, G$^+$, and G$^-$, respectively, represent trans, gauche-plus and gauche-minus conformations around the CSCC segment; t, g$^+$, and g$^-$, respectively, represent trans, gauche-plus and gauche-minus conformations around the SCCC segment; t′, g′$^+$, and g′$^-$, respectively, represent trans, gauche-plus and gauche-minus conformations around the CCCC segment. See Figure 3 for structures. [b] Dihedral angels (in deg). [c] In Hartrees. [d] Relative Gibbs energy difference (in kcal/mol). [e] Percent population based on Gibbs energies.

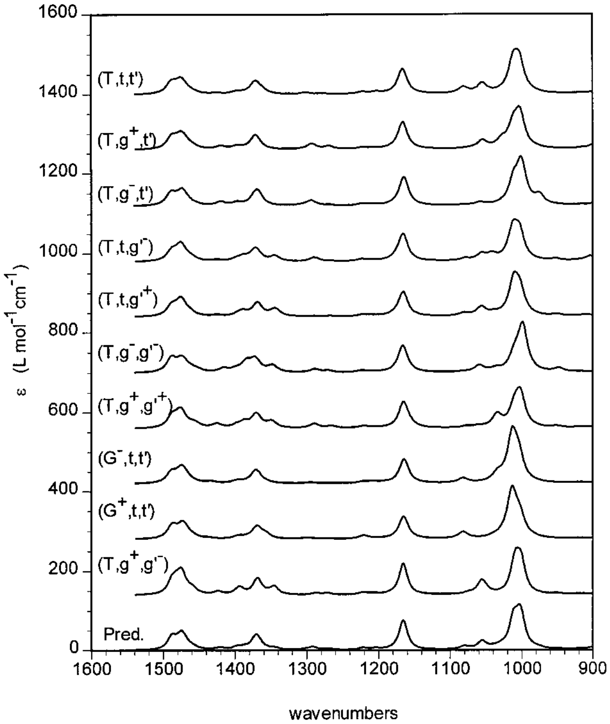

Figure 4. Ab initio vibrational absorption spectra for 10 conformers of (*R*)-*n*-butyl *tert*-butyl sulfoxide **1** obtained with B3LYP/6-31G* basis set. The spectra were simulated with Lorentzian band shapes and 8 cm^{-1} half-widths, and frequencies were multiplied with 0.96. The labels on the traces are the conformation labels (Figure 3). The predicted spectrum (bottom trace) is obtained by adding the population weighted absorption spectra of all conformers.

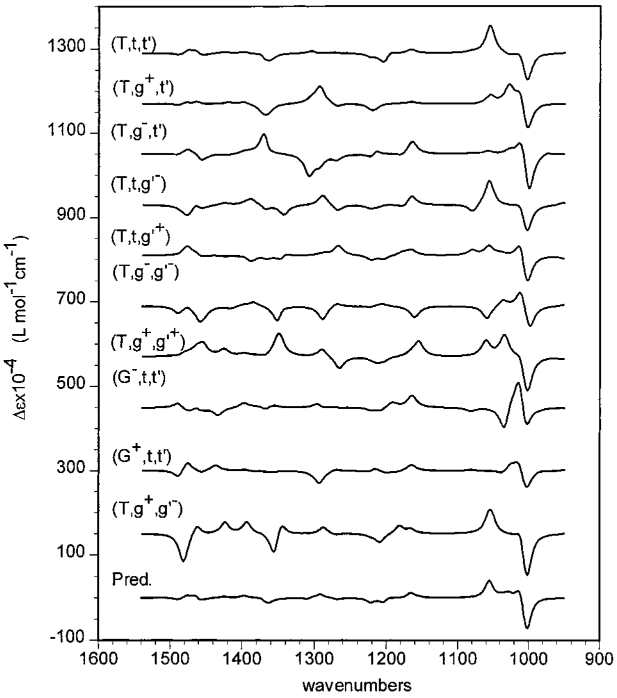

Figure 5. Ab initio VCD spectra for 10 conformers of (*R*)-*n*-butyl *tert*-butyl sulfoxide **1** obtained with B3LYP/6-31G* basis set. The spectra were simulated with Lorentzian band shapes and 8 cm^{-1} half-widths, and frequencies were multiplied with 0.96. The labels on the traces are the conformation labels (Figure 1). The predicted spectrum (bottom trace) is obtained by adding the population weighted VCD spectra of all conformers.

calculated for the 10 lowest energy conformations at the B3LYP/6-31G* level. The predicted absorption and VCD spectra simulated with 8 cm^{-1} half widths and Lorentzian band shapes are shown in Figures 4 and 5. These theoretical spectra can be compared to the experimental spectra in Figures 6 and 7.

The experimental absorption spectrum at 0.823 M is shown in Figure 6. The absorption bands in the predicted, population weighted spectrum show one-to-one correspondence with the absorption bands in experimental spectrum. The notable differences are that; (a) the two well separated experimental bands at 1163 and 1184 cm^{-1} correspond to one relatively strong band at 1165 cm^{-1} in the predicted spectrum; (b) the relative intensities of the two experimental absorption bands at 1014 and 1026 cm^{-1} are predicted to be reversed in the simulated spectrum; and (c) the predicted bands corresponding to the weak experimental absorption band at 1381 and 1051 cm^{-1} are not resolved in the simulated spectra. Except for these differences the experimental spectrum in $CDCl_3$ solution is considered to be in good agreement with the predicted absorption spectrum.

The experimental VCD spectra of (+) *n*-butyl *tert*-butyl sulfoxide (**1**) obtained at two different concentrations, 0.823 M (for the 1600−1150 cm^{-1} region) and 0.421 M are shown in Figure 7. The significant VCD bands in the observed spectra are a positive band at 1067 cm^{-1} and a positive-negative couplet with positive maximum at 1028 cm^{-1} and negative maximum at 1014 cm^{-1}. The same

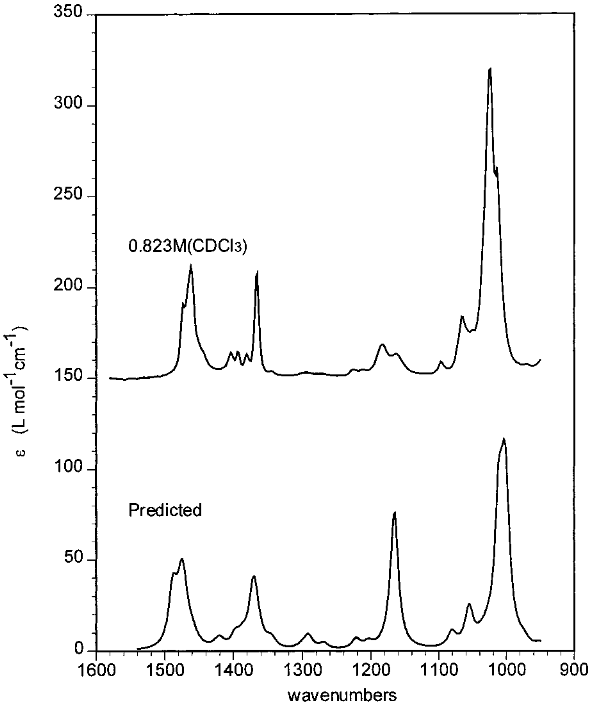

Figure 6. Comparison of the experimental absorption spectra of (*R*)-*n*-butyl *tert*-butyl sulfoxide **1** at 0.823 M with the predicted absorption (bottom trace) obtained with B3LYP/6-31G* basis set. The spectra were simulated with Lorentzian band shapes and 8 cm^{-1} half-widths, and frequencies were multiplied with 0.96.

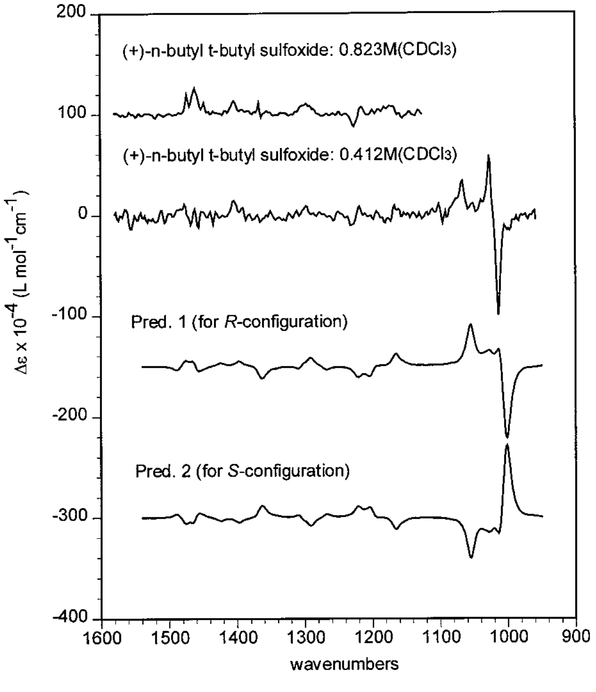

Figure 7. Comparison of the experimental VCD spectra of (+)-*n*-butyl *tert*-butyl sulfoxide at 0.412 M and 0.823 M (~1600−1150 cm^{-1}) with the predicted VCD of (*R*)-*n*-butyl *tert*-butyl sulfoxide (Pred. 1) and (*S*)-*n*-butyl *tert*-butyl sulfoxide (Pred. 2) obtained with B3LYP/6-31G* basis set. The spectra were simulated with Lorentzian band shapes and 8 cm^{-1} half-widths, and frequencies were multiplied with 0.96.

features are seen in the predicted VCD spectrum of (*R*)-*n*-butyl *tert*-butyl sulfoxide (Pred. 1) with positive band at 1055 cm^{-1} and a positive-negative couplet with positive portion resolved into two positive bands (at 1014 and 1028 cm^{-1}) and negative maximum at 1001 cm^{-1}. The relative intensity for the positive portion of this couplet is somewhat lower than that seen in the experimental VCD spectrum. The weak VCD bands present in the simulated spectrum in the 1500−1100 cm^{-1} region do not have corresponding VCD bands in the experimental spectrum at 0.412 M. But some of these features become apparent in the spectrum obtained at a higher absorbance using higher concentration. Nevertheless, these bands are weak enough to be of further interest; the major VCD features observed for (+)-*n*-butyl *tert*-butyl sulfoxide **1** are reproduced in the predicted VCD spectrum for (*R*)-*n*-butyl *tert*-butyl sulfoxide (**1**). The predicted spectrum for (*S*)-*n*-butyl *tert*-butyl sulfoxide (**1**) has opposite signs from those observed for (+)-*n*-butyl *tert*-sulfoxide (**1**). Hence (*R*)-configuration should be assigned to (+)-enantiomer.

Conclusion

The absolute configuration (*R*) of (+)-*n*-butyl *tert*-butyl sulfoxide (**1**) was determined by chemical correlation involving alkylation of the α-carbanion derived from (*R*)-(−)-*tert*-butyl methyl sulfoxide (**4**) with *n*-propyl bromide. A definitive proof of the absolute configuration of the title, enantiomeric sulfoxides **1** was provided by X-ray crystallography of the crystalline complex obtained from the enantiomerically pure (−)-**1** and mercury chloride. The result of X-ray analysis established that the configuration at the sulfur center in the complex is (*S*). In this way we confirmed the previous assignments to the enantiomeric sulfoxides **1** proposed by Kagan and Evans. Hence, our conclusion regarding the steric course (retention) of the reaction of the sulfinate **3** with *tert*-buylmagnesium chloride (Scheme 1) calls for correction.

It was demonstrated that chiral sulfoxides can be studied using a combination of experimental and ab initio vibrational circular dichroism (VCD) investigations since such molecules do show significant VCD signals. The comparison of experimental and ab initio predicted absorption and VCD spectra indicated that (+)-**1** has the (*R*) absolute configuration and exists in different conformations in the $CDCl_3$ solution.

Experimental Section

All melting and boiling points were uncorrected. ^{1}H NMR spectra were recorded at 200 and 300 MHz. Optical rotation measurements were made with an automatic photopolarimeter (sensitivity ± 0.002°). TLC was done on silica gel (Merck Silica 60 F_{254}) and column chromatography on Merck Silica gel 230−400 mesh. Solvents and commercial reagents were distilled and dried by conventional methods before use. All moisture sensitive reactions were carried out in a dry argon atmosphere.

Measurements. The infrared and VCD spectra were recorded on a commercial Fourier transform VCD spectrometer. The VCD spectra were recorded with 1 h data collection time at 4 cm^{-1} resolution. Spectra were measured in $CDCl_3$ solvent at 0.412 and 0.823 M at path length of 140 μm. The sample was held in a variable path length cell with BaF_2 windows. In the presented absorption spectra, the solvent absorption was subtracted out. In the presented VCD spectra the raw VCD spectrum of the solvent was subtracted.

Calculations. The ab initio vibrational frequencies, absorption and VCD intensities for (*R*)-*n*-butyl *tert*-butyl sulfoxide **1** were calculated using Gaussian 98 program[16] on a Pentium II 300 MHz PC. The calculations used the density functional theory with B3LYP functional[14,17] and 6-31G* basis set.[18] A larger calculation using B3LYP/6-311G (2d, 2p) was also done for one conformer and the results found to be identical to those obtained in B3LYP/6-31G* calculation. The procedure for calculating the VCD intensities using DFT theory is due to Cheeseman et al.[15] as implemented in Gaussian 98 program.[16] The theoretical absorption and VCD spectra were simulated with Lorentzian band shapes and 8 cm^{-1} full width at half-height. Since the ab initio predicted band positions are higher than the experimental values, the ab initio frequencies were scaled with 0.9613.

Akylation of (−)-(*R*)-*tert*-Butyl Methyl Sulfoxide (4): Preparation of (+)-(*S*)-*n*-Butyl *tert*-Butyl Sulfoxide (1). To a stirred solution of diisopropylamine (0.74 g, 7.3 mmol) in 50 mL of dry THF was added a solution of *n*-butyllithium (8 mmol; 5 mL of 1.6 M solution in hexane) at −70 °C. During the next 20 min the reaction mixture was slowly warmed to −10° C. Next, the reaction flask was again cooled to −70 °C, and at this temperature (−)-(*R*)-*tert*-butyl methyl sulfoxide (**4**) [0.8 g, 6.6 mmol, $[\alpha]_{589}$= −1.45 (2.1 $CHCl_3$)] was added dropwise. After the temperature was allowed to slowly warm to ca. 10° C over 30 min, the reaction mixture was then cooled to −70° C and *n*-propyl bromide (0.861 g, 7 mol) then added dropwise. The cooling bath was removed, and the reaction mixture was stirred for an additional 60 min. During this period, the reaction flask reached room temperature. The reaction mixture was poured to a 2% molar solution of ammonium chloride. The water phase was removed and extracted with chloroform. The combined chloroform extracts were washed with a saturated solution of potassium carbonate and water and dried over anhydrous magnesium sulfate. After evaporation of the solvent the crude reaction product (1 g) was purified by column chromatography on silica gel using a mixture of hexanes−ethyl ether as eluent. The analytically pure sulfoxide **1** (0.50 g, 49% yield) had $[\alpha]_{589}$ = +12.3 (2.15, acetone). Its spectral ^1H and ^{13}C NMR data fully supported the structure.

Reaction of Optically Active *n*-Butyl *p*-Tolyl Sulfoxide (2) with *tert*-Butyllithium: Preparation of (−)-*n*-Butyl *tert*-Butyl Sulfoxide (1). A three-neck round-bottom flask was charged with optically active sulfoxide **2** (0.320 g, 1.63 mmol; the values of optical rotation are given in Table 1) and ethyl ether (35 mL) and cooled to −70 °C. A solution of *tert*-butyllithium (6.5 mmol) in hexane was injected rapidly at this temperature and the reaction mixture was kept at −70° C for additional 30−60 min. The reaction mixture was poured to water and the water phase was extracted with chloroform. The combined organic phases were dried over anhydrous magnesium sulfate. The solvent was evaporated and the crude product was chromatographed on a silica gel (230−400 mesk) column with a mixture hexanes−ethyl ether as an eluent. The analytically pure sulfoxides **1** were isolated in 45−72% yields and had optical rotations given in Table 1. Their ^1H NMR spectra were in full agreement with those reported for the structure **1**.[23]

Synthesis of the Mercury Chloride Complex with the Enantiomerically Pure, Levorotatory Enantiomer of *n*-Butyl *tert*-Butyl Sulfoxide (1). To a solution of (−)-*n*-butyl *tert*-butyl sulfoxide (**1**) [50 mg, 0.3 mmol, $[\alpha]_{589}$ = −126.6 (2.3, acetone)] in dry acetonitrile (10 mL) was added mercury chloride (90 mg, 0.3 mmol). The solvent was removed by evaporation on a water pump. The residue was dissolved in a mixture of acetonitrile (5 mL) and benzene (10 mL). The solvents were allowed to evaporate very slowly at room temperature. After 10 days, suitable crystals of the complex (−)-**1**·$HgCl_2$ having $[\alpha]_{589}$= −100 (0.4, CH_3CN) were collected for the X-ray analysis.

Table 3. Crystal Data and Experimental Details

molecular formula	$4 \cdot C_8H_{18}OS + 5 \cdot HgCl_2$
space group	*P*1
a (Å)	9.036(2)
b (Å)	12.482(2)
c (Å)	13.384(3)
α (°)	84.7993)
β (°)	83.16(3)
γ (°)	82.87(3)
V ($Å^3$)	1482.8(5)
Z	1
D_c (g/cm^3)	2.247
μ (cm^{-1})	135.17
crystal dimensions (mm)	0.25, 0.25, 0.25
maximum 2*θ* (°)	54
radiation, *λ* (Å)	Mo Kα, 0.71069
scan mode	*ω*/2*θ*
scan width (°)	1.35 + 0.35·tan *θ*
hkl ranges, *h* =	0, 9
k =	−14, 14
l =	−15, 15
no. of reflections:	
unique	3863
with $I \geq 4\sigma(I)$	2504
no. of parameters refined	499
largest diff. peak (e $Å^{-3}$)	3.211
largest diff. hole (e $Å^{-3}$)	−2.058
R_{obs}	0.0665
R_w,obs	0.0646
weighting coeff.,[a] *m*	0.009876
extinction coeff.,[b] *k*	0.00006(4)
S	0.8219
shift/esd max	0.059
R_{int}	0.078
T_{meas}	293(2)
F(000)	930
absolute structure	$S_{S1a,b,c,d}$
Rogers parameter *η*	1.02(2)

[a] Weighting scheme $w = [\sigma^2(F) + mF^2]^{-1}$. [b] Extinction method XLS, extinction expression $F_c^* = F_c[1 + 0.002kF_c^2/\sin(2\theta]^{-1/4}$.

Crystal Structure of the Mercury Chloride Complex with (−)-*n*-Butyl *tert*-Butyl Sulfoxide (1). The crystal and molecular structures of (−)-**6** were determined using data collected on a CAD4 diffractometer. The complex crystallizes in triclinic system, in space group P1. The unit cell constitutes four molecules of *n*-butyl *tert*-butyl sulfoxide (**1**) and five of $HgCl_2$. Crystal data and experimental details, non-hydrogen atomic coordinates and equivalent isotropic displacement coefficients are shown Table 3. Intensity data were collected at room temperature using diffractometer with graphite monochromatized Mo Kα radiation. Lattice constants were refined by least-squares fit of 25 reflections in *θ* range 10−19°. A total of 2504 observed reflections (with $I \geq 4\sigma(I)$) were used to solve the structure by direct methods and to refine it by full matrix least-squares using *F*'s. Hydrogen atoms were placed geometrically and set as riding with isotropic thermal parameters set to 0.097 and not refined. Anisotropic thermal parameters were refined for all nonhydrogen atoms. The final refinement converged to *R* = 0.0665 with weight $1/(\sigma^2(F) + 0.009876F^2)$ for 499 refined parameters, with inclusion of extinction parameter into refinement (the obtained value of extinction parameter was 0.00004(4)).

Structure solution was carried out with the Enraf-Nonius SDP crytallographic computing package[19] and SHELXS-86 program;[20] structure refinement with SHELXTL package.[21] Scattering factors were taken from *International Tables for X-ray Crystallography*.[22] Full crystallographic data, with values of F_{obs} and F_{calc}, are deposited at the Cambridge Crystallographic Data Centre.[24]

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Synthesis of (+)-*tert*-Butyl *n*-Butyl Sulfoxide. (+)-**1** was prepared for VCD studies at Vanderbilt, from (S)-(−)-1,1-diphenyl-1,2-propanediol cyclic sulfite (Aldrich) using Anderson method as described by Kagan et al.:[5] $[\alpha]^{23}_{D}$ +70° (2.0, $CDCl_3$). Its ^1H spectra fully supported the structure.

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Supporting Information Available: Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-H atoms; anisotropic displacement coefficients (Å^2) for non-hydrogen atoms; bond lengths (Å) for non-hydrogen atoms; bond angles (deg) for non-hydrogen atoms; torsional angles (deg) for non-hydrogen atoms; hydrogen-bonding geometry (Å, deg) (H···A not greater than 2.80 Å); environment of Hg. This material is available free of charge via the Internet at http://pubs.acs.org.

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