X-Ray Study of (α*S*,*SS*/α*R*,*SR*)-1-(*p*-Bromophenyl)ethyl t-Butyl Sulphoxide and Conformational Analysis of Diastereoisomeric Pairs of 1-Phenylethyl t-Butyl Sulphoxides

By **Yoshio Kodama**, **Ken Nishihata**, and **Motohiro Nishio**,* Central Research Laboratories, Meiji Seika Kaisha Ltd., Morooka, Kohoku, Yokohama 222, Japan
Yoichi Iitaka, Faculty of Pharmaceutical Sciences, University of Tokyo, Tokyo 113, Japan

The title compound, $C_{12}H_{17}BrOS$, is monoclinic, space group $P2_1/n$, a = 12.87(1), b = 6.005(6), c = 17.32(2) Å, β = 90.37°, Z = 4, D_m = 1.434 g cm^{-3}. The structure was solved by the heavy-atom method and refined to an R value of 0.09. It has been shown that the bulkiest group (Bu^t) orients itself *anti* to the methyl group and *gauche* to the phenyl group. Solution phenomena (n.m.r. and o.r.d.–c.d. data) of some diastereoisomeric pairs of 1-phenylethyl t-butyl sulphoxides are best interpreted by assuming that the predominant conformations of these molecules resemble those found in *X*-ray crystallographic studies.

ANOMALIES observed in the product analysis,[1] n.m.r. solvent [1e] and shift reagent effects,[2] and rotatory dispersion (r.d.) properties of diastereoisomeric 1-phenylethyl alkyl (or aryl) sulphoxides prompted us to examine, by *X*-ray analysis, the conformation of (*RS*) † and (*SR*)-1-(*p*-bromophenyl)ethyl t-butyl sulphoxide (I). We found that the bulkiest group (t-butyl) is oriented *gauche* to the phenyl group.[1b] To explore the generality of this conformation we have now determined by *X*-ray analysis the structure of the racemic (*RR*/*SS*) congener of the above compound and studied the n.m.r. and the r.d. properties of the relevant molecules.

This paper establishes that, at least in the presently studied compounds, the achiral group prefers to orient itself *gauche* and *anti* to the phenyl and the methyl groups, respectively, not only in the solid state but also in solution. N.m.r.[1e,2] and r.d. characteristics of the diastereoisomeric pairs were very puzzling while a *trans*-arrangement of the apparently bulkier groups was assumed, but are reasonably interpreted on the basis of the above conformation. This requires that the bulky achiral group (t-butyl in the present case) is flanked by the least bulky hydrogen atom and the phenyl group (allegedly bulkier than methyl), an unusual circumstance from considerations of steric factors as commonly considered.

EXPERIMENTAL

N.m.r. spectra were determined for 0.2mM solutions in carbon tetrachloride on a Varian XL-100 instrument. Chemical shifts are given relative to tetramethylsilane (δ 0) as internal reference and are accurate to ±0.01 p.p.m.

---

† The correct sequence rule symbol is (α*R*,*SS*) for this configuration. Abbreviated forms are used in the paper for the sake of brevity.

[1] (*a*) K. Nishihata and M. Nishio, *J.C.S. Perkin II*, 1973, 758; (*b*) Y. Iitaka, Y. Kodama, K. Nishihata, and M. Nishio, *J.C.S. Chem. Comm.*, 1974, 389; (*c*) D. J. Cram and S. H. Pine, *J. Amer. Chem. Soc.*, 1963, **85**, 1096; (*d*) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simons, and A. L. Ternay, jun., *ibid.*, 1965, **87**, 1958; (*e*) M. Nishio, *Chem. Comm.*, 1969, 51; M. Nishio and K. Nishihata, *ibid.*, 1970, 1485.

[2] R. R. Fraser, T. Durst, M. R. McClory, R. Viau, and Y. Y. Wigfield, *Internat. J. Sulfur Chem.* (*A*), 1971, **1**, 133 and references cited therein.

O.r.d. and c.d. spectra were determined for ethanol and iso-octane solutions with a JASCO ORD/CD-5 automatic recording spectrophotometer. The reported values are corrected to the optical purity of the starting (*R*)-(+)-benzyl t-butyl sulphoxide (75% optically pure). Optical rotations were determined in ethanol.

Preparations of Racemic Sulphoxides.—(*RS*/*SR*)-(I), m.p. 103°, and (*RS*/*SR*)-1-phenylethyl t-butyl sulphoxide (II), m.p. 56°, were prepared as reported.[1b] (*RR*/*SS*)-(I), m.p. 98°, and (*RR*/*SS*)-(II), m.p. 70°, were prepared by *O*-alkylation of their diastereoisomeric congeners with triethyloxonium fluoroborate followed by alkaline hydrolysis.[3]

X-*Ray Structure Determination*.—Crystals of (*RR*/*SS*)-(I) are monoclinic, space group $P2_1/n$, $a = 12.87(1)$, $b = 6.005(6)$, $c = 17.32(2)$ Å, $\beta = 90.37°$, $Z = 4$, $D_m = 1.434$ g cm^{-3}. Three-dimensional intensity data were collected with Cu-K_α radiation on an automatic four-circle diffractometer. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares analysis. Full details of the *X*-ray results will appear in a forthcoming paper.

(R)-(+)-*Benzyl t-Butyl Sulphoxide* (III).—(−)-Menthyl phenylmethanesulphinate[4] (0.35 mol), $[\alpha]_D$ +116°, was treated with an ethereal solution of t-butylmagnesium chloride (0.7 mol) and the resulting sulphoxide was purified by silica gel chromatography (eluant, petroleum, light petroleum, and then ether). The sulphoxide (III) (35 g) obtained from the ethereal fractions, $[\alpha]_D$ +130°, was recrystallized three times from ligroin giving crystals (9 g), m.p. 75°, $[\alpha]_D$ +212° (75% optically pure[4]), δ (CCl_4) 1.25 (9 H, s), 3.56 (2 H, q, δAB 0.20 p.p.m., *J* 12.5 Hz), and 7.26br (5 H, s); $\nu_{max.}$ (Nujol) 1 056 cm^{-1} (S–O).

(SR)-1-*Phenylethyl t-Butyl Sulphoxide* (IV).—Compound (III) was treated in tetrahydrofuran (THF) with Bu^{n}Li (1.1 equiv.) at −70° under nitrogen and then quenched with excess of methyl iodide. N.m.r. analysis of the resulting crude material failed to detect any trace of (*RR*)-(IV), the diastereoisomeric congener of the expected product. Recrystallization from ligroin gave (*SR*)-(IV), m.p. 85°, $[\alpha]_D$ −122°, in 86% isolated yield. P.l.c. (silica gel; n-hexane–ether 1 : 3) of the mother liquor gave 6% (*SR*)-(IV), $[\alpha]_D$ −70°, and 0.5% (*RR*)-(IV), $[\alpha]_D$ +122°. Thus the selectivity of the reaction is nearly 99.5%.

(RR)-1-*Phenylethyl t-Butyl Sulphoxide* (IV)—A THF solution of (*SR*)-(IV) was treated with Bu^{n}Li (1.1 equiv.) at −70° and quenched, after standing for 0.5 h, with excess of water. N.m.r. analysis of the material revealed that it consisted of *ca.* 90% (*RR*)-(IV) (inverted at the carbon atom) and 10% (*SR*)-(IV). Recrystallization from ligroin gave (*RR*)-(IV) (70%), m.p. 105°, $[\alpha]_D$ +158°. The remaining sulphoxides in the mother liquor were separated by p.l.c. to afford 13% of (*RR*)-(IV) and 8% of (*SR*)-(IV).

(RS)-1-*Phenylethyl t-Butyl Sulphoxide* (IV).—Treatment of a methylene chloride solution of (*RR*)-(IV) with triethyloxonium fluoroborate gave the *O*-ethoxysulphonium salt of the sulphoxide. This was treated with 0.1N-NaOH to afford the inverted sulphoxide, (*RS*)-(IV), m.p. 88°, $[\alpha]_D$ +136°, in 81% isolated yield.

Compound (*SS*)-(IV), m.p. 105°, $[\alpha]_D$ −155°, was prepared from (*RS*)-(IV) as in the preparation of (*RR*)-(IV) from (*SR*)-(IV). Compound (*SR*)-(IV), m.p. 89°, $[\alpha]_D$ −144°, was obtained by the treatment of (*SS*)-(IV) with Meerwein's reagent followed by alkaline hydrolysis, thus completing a stereochemical cyclic procedure illustrated in the text. All of the stereoisomers described gave correct elemental analysis.

Recovery Experiment (*Proof of the Configurational Stability of the* S–O *Bond in the Butyl-lithium Treatment*).—A THF solution (0.78 g in 50 ml) of (*R*)-(+)-(III), $[\alpha]_D$ 254°, was treated with excess of Bu^{n}Li at −70° under an inert atmosphere. After standing for 0.5 h, this was quenched with water. Work-up on the recovered sulphoxide gave crystals (0.7 g) with $[\alpha]_D$ +248°. The n.m.r. and i.r. spectra were identical to those of the starting material.

RESULTS AND DISCUSSION

The structure of the (*SS*)-enantiomer of (I) for an *R* factor of 9% is shown in Figure 1. It is clear that the bulkiest group, Bu^t, orients itself *gauche* to the phenyl group, the torsion angles between Bu^t and Ph, Ph and O, and O and Me^4 being *ca.* 65, 50, and 72°, respectively.

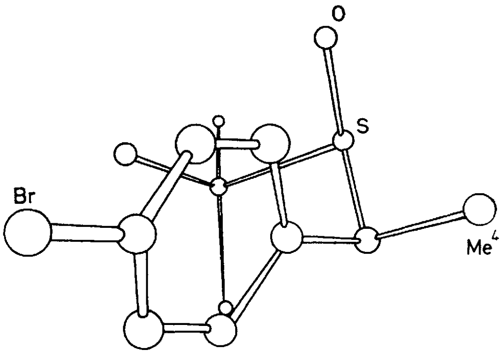


FIGURE 1 Crystal structure of (α*S*,*SS*)-1-(*p*-bromophenyl)-ethyl t-butyl sulphoxide

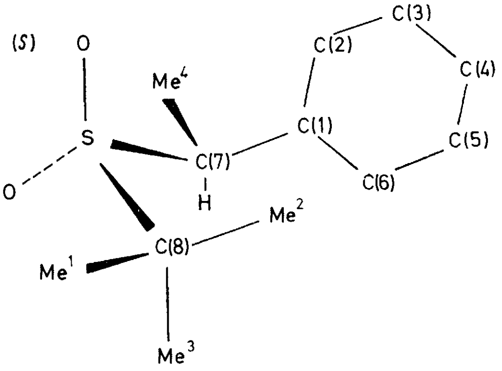


FIGURE 2 Combined diagram for the crystallographic structures of (α*S*,*SS*)- and (α*S*,*SR*)-1-(*p*-bromophenyl)ethyl t-butyl sulphoxides

TABLE 1

Some interatomic distances (Å) in (*SR*)-(I) and (*SS*)-(I)

	(*SR*)	(*SS*)
C(2)–C(Me^2)	3.7	3.6
C(6)–C(Me^2)	3.7	3.7
C(3)–C(Me^2)	4.4	4.2
C(5)–C(Me^2)	4.3	4.3
O–C(Me^4)	3.0	3.2

Figure 2 combines the results of the *X*-ray studies of the (*SS*)- and (*SR*)-isomers[1b] and Table 1 lists some structural parameters of these two compounds.

---

[3] C. R. Johnson and D. M. McCants, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 5404.

[4] K. Mislow, M. M. Green, and M. Raban, *J. Amer. Chem. Soc.*, 1965, **87**, 2761.

It is found in both compounds that the Me^4 group in the chiral cluster is practically coplanar with the Me^1–C(8)–S–C(7)–Me^4 sequence of atoms and the phenyl group is close to one of the two remaining Me groups (Me^2) of the t-butyl group. The dihedral angles defined by C(Me^2)–C(8)–C(7)–C(1) are *ca.* 7 and *ca.* 11° in (*SR*)- and (*SS*)-(I), respectively. The phenyl group rotates about the connecting bond to present its smallest van der Waals dimension to the adjacent methyl (Me^2). Thus the interatomic distance from Me^2 to C(2) equals that from Me^2 to C(6). The substructure of the t-butyl group vanishes in solution, however, since there is a sharp singlet in the n.m.r. spectrum. It follows that the S–C(Bu^t) bond rotates freely and the three methyl groups are equivalent in solution, at least at room temperature.

We suggest that a factor which favours the *gauche*-conformation is the effective bulk of the methyl group (Me^4), the three hydrogen atoms on it repelling the three methyls of the t-butyl group.* Thus no rotations about $CH-CH_3$ and $S-C(CH_3)_3$ bonds can relieve this interaction. Interactions of the t-butyl with the planar phenyl group, on the other hand, can easily be reduced by a rotation about the C–C(Ph) bond.

N.m.r. parameters of racemic sulphoxides, (*RS*/*SR*)-(I) and -(II), and (*RR*/*SS*)-(I) and -(II), are listed in Table 2.

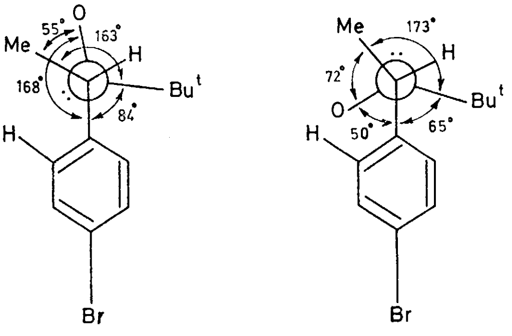
TABLE 2

N.m.r. chemical shift data

	(*RS*/*SR*)-(I)				(*RR*/*SS*)-(I)				(*RS*/*SR*)-(II)				(*RR*/*SS*)-(II)			
	CH	Me	*o*-H	Bu^t	CH	Me	*o*-H	Bu^t	CH	Me	*o*-H	Bu^t	CH	Me	*o*-H	Bu^t
CCl_4	3.72	1.49	7.13	1.09	3.64	1.64	7.20	1.02	3.75	1.55	7.24	1.07	3.64	1.71	7.26	0.97
ASIS [a]	+0.31	+0.10			+0.43	+0.27			+0.17	+0.01			+0.30	+0.23		
ΔEu [b]	−2.15	−2.22	−0.71	−1.45	−0.91	−1.26	−1.24	−1.03	−2.12	−2.22	−0.66	−1.41	−0.82	−1.21	−1.13	−0.98

[a] $\delta(CCl_4) - \delta$(benzene). [b] Shifts observed in CCl_4 containing $Eu(fod)_3$ (0.2 equiv.).

These data are consistently interpreted by assuming that the predominant conformers in solution resemble those illustrated in Figure 3 (Newman projections of the *X*-ray results), and that the effects of aromatic solvents and shift reagents are like those established by studies on cyclic sulphoxides.[5] Thus larger benzene-induced shifts were observed for both CH and Me signals of the (*RR*/*SS*)-isomer, whereas larger paramagnetic reagent-induced shifts were observed for the CH and Me peaks in the (*RS*/*SR*)-sulphoxides. The peaks appropriate to the *ortho* protons in the aromatic ring (*o*-H) of (*RR*/*SS*)-(I) and -(II) are significantly more sensitive to the addition of paramagnetic species than those of (*RS*/*SR*)-(I) and -(II), respectively. Further support comes from the fact that the singlets attributed to the t-butyl group in the above compounds (δ 0.97—1.09, see Table 2) are significantly shielded compared with those for Bu^t in benzyl t-butyl sulphoxide (δ 1.25). This is a logical consequence from the expectation that the three methyl groups on Bu^t in the former should experience the anisotropic shielding effect of the proximate aromatic ring. In the latter compound which lacks the Me–Bu^t interaction, on the other hand, the t-butyl group is assumed to be oriented *trans* to the phenyl group.† The differences in ΔEu of the t-butyl signals observed between the diastereoisomeric pairs [−1.45 *vs.* −1.03 for (I) and −1.41 *vs.* −0.98 for (II)] are also consistent with the *X*-ray results, the bond angle O–$\widehat{S}$–C(Bu^t) being smaller (103°) in (*SR*)-(I) than in (*SS*)-(I) (108°).



(*SR*)-(I) (*SS*)-(I)

FIGURE 3

The fact that all the n.m.r. data obtained from these sets of sulphoxides are self-consistent, irrespective of whether CH, Me, *o*-H, or Bu^t is used as probe, suggests that these molecules, at least qualitatively, are conformationally frozen in solution as indicated in Figure 3.‡

All the optically active diastereoisomers of 1-phenylethyl t-butyl sulphoxide (IV) were prepared according to the procedures shown in the Scheme. Thus, treatment of (*R*)-benzyl t-butyl sulphoxide (III)[4] with Bu^{n}Li followed by quenching with MeI gave almost exclusively (*SR*)-(IV).[1b,6] This is a kinetically controlled process, since (*SR*)-(IV) was converted to a *ca.* 9 : 1 mixture of

---

* For some recent concepts regarding van der Waals interactions or the effective bulk of groups in conformational analysis, see D. R. Wertz and N. L. Allinger, *Tetrahedron*, 1974, **30**, 1579.

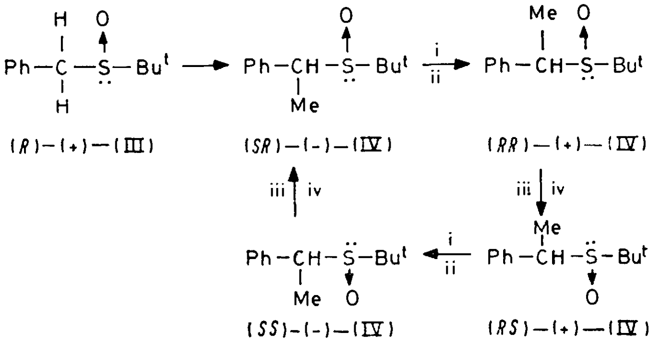
† An inspection of models (see Figure 3) suggests that Bu^t in (*RR*/*SS*)-sulphoxides should be more shielded (by the ring current effect) than in (*RS*/*SR*)-isomers. This also is borne out by the n.m.r. data: δ 1.02 *vs.* 1.09 for (I) and 0.97 *vs.* 1.07 for (II).

‡ We do not wish to imply that perturbations to the conformational equilibria are negligible. Insight into the situation, however, seems to be provided by the simple premises mentioned. This is supported by the relative insensitivity of the r.d. characteristics of these compounds to change of solvent and to addition of shift reagent.

[5] S. Bory, R. Lett, B. Moreau, and A. Marquet, *Tetrahedron Letters*, 1972, 4921; R. R. Fraser and Y. Y. Wigfield, *Chem. Comm.*, 1970, 1471 and references cited therein.

[6] T. Durst, R. Viau, and M. R. McClory, *J. Amer. Chem. Soc.*, 1971, **93**, 3077.

(*RR*)- and (*SR*)-(IV) after thermodynamic equilibrium (contact with Bu^nLi followed by quenching with water).



SCHEME Reagents: i, 1.1 equiv. of Bu^nLi in THF; ii, H_2O; iii, $Et_3O^+BF_4^-$ in CH_2Cl_2; iv, 0.1 N-NaOH

Compound (*RR*)-(IV), after purification, was converted into (*RS*)-(IV) *via* its *O*-ethoxysulphonium salt.[3] This was converted to (*SS*)-(IV) and (*SR*)-(IV) was finally recovered by treating (*SS*)-(IV) with Meerwein's reagent followed by alkaline hydrolysis of the salt.

TABLE 3

$Eu(tfc)_3$-Induced chemical shift

	CCl_4	$\delta Eu(tfc)_3$ [a]	$\Delta Eu(tfc)_3$ [b]
(*SR*)	1.07	1.75	−0.68
(*RS*)	1.07	1.71	−0.64
(*RR*)	0.97	1.31	−0.34
(*SS*)	0.97	1.21	−0.24

[a] 0.1mM Solutions in CCl_4 containing $Eu(tfc)_3$ (0.2 equiv.).
[b] $\delta(CCl_4) - \delta[Eu(tfc)_3]$.

perfect recovery of the optical activity of the starting sulphoxide, (*R*)-(III), on treatment with Bu^nLi followed by quenching with water. The configurations of these sulphoxides were further confirmed by n.m.r. measurements with use of a chiral shift reagent, tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium, $Eu(tfc)_3$. Table 3 lists the shifts induced by this reagent for the t-butyl peaks.

Differences in $\Delta Eu(tfc)_3$ are small between (*SR*)- and (*RS*)-, and (*RR*)- and (*SS*)-isomers, but they are sufficient for differentiating these sets of enantiomeric sulphoxides.

Tables 4 and 5 list the o.r.d. and c.d. characteristics of (*R*)-(+)-benzyl t-butyl sulphoxide (III)[7] and the optically active isomers of 1-phenylethyl t-butyl sulphoxide (IV).

All the compounds examined here give rise to r.d. curves with a Cotton effect extremum at 238—242 nm in ethanol and at 250—252 nm in iso-octane. The red shift observed in the non-polar solvent indicates that the associated transition is n–π^* in type.[1d]

Compounds (*R*)-(III) and (*RR*)-(IV) show o.r.d. curves with positive Cotton effects in ethanol and they are not influenced by change of solvent polarity, although reduction in the molecular amplitude (as well as the red shift) was observed in iso-octane for both compounds. Most interesting, however, was that (*SR*)-(IV) displays negative Cotton effect at the corresponding wavelengths in both solvents. This is illustrated in Figure 4. Note that these three compounds have the same chirality (*R*) at sulphur. This strongly suggests that the relative spacial orientation of phenyl with respect to the chiral centre is quite different in these diastereoisomers.

TABLE 4

O.r.d. characteristics of (*R*)-benzyl t-butyl sulphoxide (III) and 1-phenylethyl t-butyl sulphoxides (IV)

	Solvent			*z*		*a*	Δ*a*
(*R*) − (+) − (III)	E	300 (+3 900)	233pk (+50 500)	224	218tr (−78 500)	+1 290	
	I	300 (+4 400)	241pk (+36 500)	233	223tr (−47 300)	+838	+452
(*SR*) − (−) − (IV)	E	300 (−4 700)	238tr (−44 600)	228	218pk (+75 200)	−1 198	
	I	300 (−11 900)	252tr (−52 900)	240	224pk (+108 000)	−1 609	+411
(*RR*) − (+) − (IV)	E	300 (+3 100)	243pk (+26 600)	233	222tr (−68 700)	+944	
	I *	300 (+2 700)	250pk (+12 300)	242	230tr (−35 300)	+476	+468
(*RS*) − (+) − (IV)	E	300 (+5 200)	238pk (+45 200)	228	218tr (−77 000)	+1 222	
	I	300 (+8 500)	252pk (+53 500)	240	224tr (−108 000)	+1 615	−393
(*SS*) − (−) − (IV)	E	300 (−3 600)	243tr (−28 800)	233	220pk (+67 000)	−958	
	I	300 (−2 900)	252tr (−15 500)	240	228pk (+35 000)	−505	−453

E = Ethanol, I = Iso-octane. Wavelengths in nm, molecular rotations [ϕ] in parentheses. pk = Peak, tr = trough, *z* = points at which the zero-rotation axis is crossed, *a* = molecular amplitude, $\Delta a = a(E) - a(I)$.

* Addition of $Eu(fod)_3$ (0.15 equiv.) gave a r.d. curve with a positive Cotton effect centred at 238 nm (*a* 482).

The conversions of (*SR*)- to (*RR*)-(IV) and of (*RS*)- to (*SS*)-(IV) were not accompanied with configurational inversion at sulphur. This was shown by the almost

By analogy with β,γ-unsaturated carbonyl compounds including open-chain ketones,[8] benzylic sulphoxides are conceived to exhibit chiroptical properties that would

---

[7] U. Folli, F. Montanari, and G. Torre, *Tetrahedron Letters*, 1966, 5037.

[8] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1945.

reflect the relative asymmetric disposition of the strongly perturbing phenyl group and the sulphinyl chromophore. The o.r.d. curves of some benzyl[7,9] and alkyl allyl sulphoxides[10] have in fact been shown to be dependent on solvent polarity perhaps due to variations of conformational equilibria. In harmony with the available evidence on conformationally restricted benzylic[11] and allylic sulphoxide[12] systems the presently studied t-butyl sulphoxides represent a conformationally restricted acyclic system,* since neither a change in the solvent polarity nor an addition of the europium shift reagent to the iso-octane solutions (see Table 4, footnote) is accompanied by such a drastic change in molecular amplitude (and of course in sign) as was observed in *e.g.*, benzyl methyl sulphoxide.[7]

TABLE 5

C.d. data of 1-phenylethyl t-butyl sulphoxides (IV)

Configuration	Solvent	λ/nm ([θ])			
(*SR*)	E	270 (0)	226 (−78 500)		
	I	280 (0)	239 (−87 900)	218 (0)	
(*RR*)	E	260 (0)	231 (+51 800)	220 (0)	215 (−38 400)
	I	270 (0)	240 (+21 300)	230 (0)	218 (−52 200)
(*RS*)	E	273 (0)	226 (+76 800)		
	I	280 (0)	238 (+90 000)	219 (0)	
(*SS*)	E	260 (0)	232 (−46 800)	221 (0)	214 (+45 200)
	I	270 (0)	243 (−22 600)	232 (0)	218 (+52 000)

E = Ethanol, I = iso-octane.

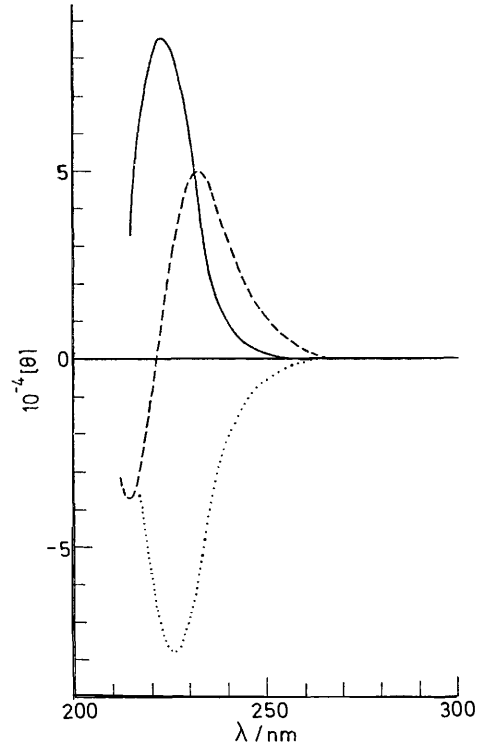


FIGURE 4 C.d.s. spectra (in ethanol) of (*R*)-(IV) (solid line), (*RR*)-(IV) (dashed line), and (*SR*)-(IV) (dotted line

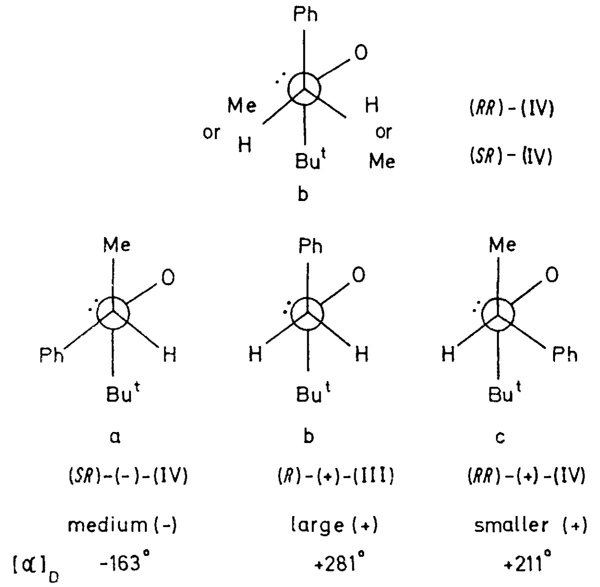


FIGURE 5 Conformations of sulphoxides (IV). $[\alpha]_D$ Values determined in ethanol and corrected for optical purity

We believe that the relative geometrical disposition of Ph with respect to S–O is rather fixed in solution and quite different in (*SR*)- and (*RR*)-(IV). *X*-Ray analyses of the diastereoisomeric pair of 1-(*p*-bromophenyl)ethyl t-butyl sulphoxide (I) have already established that the sulphinyl group in (*RS*/*SR*)- and (*RR*/*SS*)-(I) is oriented *anti* and *gauche*, with respect to the phenyl group as shown in Figures 5a and c, respectively. The two conformations a and c correspond, therefore, to the negative and positive sign of the Cotton effect, and we suggest that the conformers a and c prevail in solutions of (*SR*)- and (*RR*)-(IV), respectively; this is fully consistent with the n.m.r. results. For both molecules the steric repulsion between Bu^t and Me, which we assume to be the dominant factor in determining the conformational population, has been avoided, whereas it occurs in b (this most likely corresponds to the positive sign) for both compounds, which probably accounts for the non-observance of b. The suggestion is supported by the fact that change in solvent polarity (from ethanol to iso-octane) is accompanied in all cases by a reduction in the value of the molecular amplitude (see Table 4). This is a logical consequence from the expectation that

---

* Osmometric determinations suggest that these sulphoxides are monomeric at this concentration.[11]

[9] M. Cinquini, S. Colonna, I. Moretti, and G. Torre, *Tetrahedron Letters*, 1970, 2773.

[10] M. Axelrod, P. Bickart, M. L. Goldstein, M. M. Green, A. Kjaer, and K. Mislow, *Tetrahedron Letters*, 1968, 3249.

[11] D. N. Jones and W. Higgins, *J. Chem. Soc.* (*C*), 1969, 2159.

[12] D. N. Jones, J. Blenkinsopp, A. C. F. Edmonds, E. Helmy, and R. J. K. Taylor, *J.C.S. Perkin I*, 1974, 937.

the proportion of conformer c, which has unfavourable electrostatic interactions, should decrease in non-polar solvents.*

The conclusion seems clear that, provided a phenyl ring can orient itself suitably relative to neighbouring atoms, such a flat, hollow ring has a smaller van der Waals dimension than a methyl group.

We thank Drs. G. Tsuchihashi (Sagami Chemical Research Centre), M. Hirota (Dept. of Chemistry, University of Yokohama), and H. Iwamura (Dept. of Chemistry, University of Tokyo) for useful discussions.

[5/2036 *Received, 20th October, 1975*]

---

* The above result will permit the assessment of the rotomeric populations of some benzylic sulphoxides where free rotation may occur.