Crystal Structure, Proton Magnetic Resonance Spectra, and Conformational Analysis of 1,4-Diphenyl-1,4-dithiabutane 1,4-Dioxides and Related Meso/*dl* and Erythro/Threo Systems

Andrew L. Ternay, Jr.,* Johnny Lin, and Thomas Sutliff

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

Shirley S. C. Chu* and Beingtau Chung

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275

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The x-ray structures for *meso-* and *dl-*1,4-diphenyl-1,4-dithiabutane 1,4-dioxide are presented. The meso isomer has a center of symmetry in the solid state. Analysis of ^{1}H NMR spectra of a series of *dl* isomers indicates that the anti conformer is present in about 75%. The erythro and threo isomers of 1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide exhibit the same anomalous ^{1}H NMR spectra (erythro, A_4; threo, AA′BB′) as do similar meso/*dl* sets. Both diastereomers of 1,4-bis(2-carbomethoxyphenyl)-1,4-dithiabutane 1,4-dioxide exhibit AA′BB′ ethano regions under some conditions. Intramolecular sulfinyl–sulfinyl associations are unimportant in these systems even at −60 °C. The *dl* isomers have higher molecular dipole moments than do meso isomers for simple ArS(O)-$CH_2CH_2S(O)Ar$ systems. The asymmetric oxidation of 1,4-bis(4-methylphenyl)-1,4-dithiabutane using (+)-peroxycamphoric acid is described as is the partial resolution of (±)-1,4-bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-dioxide using (−)-cinchonidine.

Because of the pyramidal stability of the sulfinyl group,[1] compounds of the type $RS(O)CH_2CH_2S(O)R$ exist as diastereomeric meso and *dl* forms while compounds of the type $RS(O)CH_2CH_2S(O)R'$ exist as diastereomeric erythro and threo forms. The first example of the preparation and separation of such compounds was reported by Bell and Bennett.[2] However, it was not until the late 1960s[3] that configurations were assigned to these diastereomers and that it was recognized that NMR spectroscopy might be used to distinguish between some simple 1,4-diaryl-1,4-dithiabutane 1,4-dioxides. Thus, it was observed that one isomer (meso) exhibited a sharp singlet for the ethano protons while the other (*dl*) exhibited the anticipated AA′BB′ spectrum. Furthermore, it was noted[3a] that this observation could not readily be extrapolated to disulfoxides of this type where R is alkyl; the ethano regions of both isomers of 2,5-dithiahexane 2,5-dioxide (**1**) and 1,4-dithiane 1,4-dioxide (**2**) all are complex multiplets.

Taddei,[3b] in assigning the meso configuration to that diastereomer of 1,4-diphenyl-1,4-dithiabutane 1,4-dioxide (**3**) which exhibited the A_4 pattern (single line) in the ethano region, suggested that this degeneracy might be due to the presence of two chiral centers of opposite chirality and the concomitant cancellation of the effects of these chiral centers upon magnetic nonequivalence. (This explanation is inconsistent with the theories[4] of the effect of chirality upon nonequivalence; both isomers should exhibit AA′BB′ patterns.) This method of configuration assignment was subsequently[5] extended to 1,4-bis(4-methylphenyl)-, 1,4-bis(4-methoxyphenyl)-, and 1,4-bis(4-acetylphenyl)-1,4-dithiabutane 1,4-dioxides (**4, 5,** and **6**, respectively), with the isomer exhibiting the singlet for the ethano region being assigned the meso structure. The results were supported[5] by partial resolution of *dl-* **3.** To date, those compounds of the type ArS(O)-$CH_2CH_2S(O)Ar$ described in the literature appear to be either A_4 (meso) or AA′BB′ (*dl*).

Taddei also suggested[3b] that (a) the anti conformer of **3** was present to an extent greater than that expected from statistical considerations and that (b) there is an usually high barrier to rotation around the ethano C–C bond in **3.** However, a quantitative assessment of population distribution was absent as was any suggestion of the origin of the supposed high barrier.

The most recent contributions to the study of these systems are in the areas of asymmetric synthesis and x-ray crystallography. Mislow and co-workers[6] have described an elegant synthesis of isomerically and enantiomerically homogeneous diaryl disulfoxides of this type. Svinning et al.[7] have published the first x-ray structure of such a compound, *meso-* **1.** Unfortunately, this x-ray analysis is (a) of only one stereoisomer and (b) of a system which behaves normally[3,4] in the NMR spectrum.

This report describes some further[3a] results from our study on the stereochemistry of these systems and begins with the single crystal x-ray analysis of *meso-* and *dl-* **3.** In this report we will show that the singlet–multiplet pattern observed for diaryl systems can be extrapolated to simple erythro–threo isomers but that not all aryl systems of this type must display this pattern. Furthermore, we will comment upon the rotomeric distribution within this type of compound and upon the solvent and temperature dependence of this distribution. Finally, we will demonstrate the application of molecular dipole moments to configurational assignment of selected disulfoxides of this type.

Results and Discussion

X-Ray Analysis.[8] The configuration of the two isomers of **3** are shown in ORTEP drawings[9] in Figure 1. In the solid state the meso isomer possesses a center of symmetry, while the two halves of the molecule of the *dl* isomer have different conformations. The differences in conformation are illustrated in Figures 2 and 3, in which are given the torsion angles about the C– S bonds in *meso-* and *dl-* **3** and *meso-* **1.** Examination of Figures 1–3 reveals that in *meso-* **3** the ArSCC fragment is gauche,gauche in both halves of the molecule, a conformation which also is observed for one half of the *dl* isomer. The other half of the *dl* isomer (ArSCC fragment) has the gauche,anti conformation. The meso isomer of **1** was found[7] to have the gauche,anti conformation for both ArSCC fragments. The torsion angles about the sulfur and aryl carbon bond (Figure 3) indicate that the phenyl ring has a partial eclipsed conformation with respect to the sulfur–oxygen bond instead of the staggered conformation of *meso-* **1.**[7] The nonbonded intramolecular distances between the oxygen and one carbon of the benzene ring in both isomers of the phenyl derivative are 2.91–2.93 Å (Figure 1). This probably is due to interaction between the phenyl group and the nonbonding electron pair on oxygen.

The bond lengths and bond angles, with their standard

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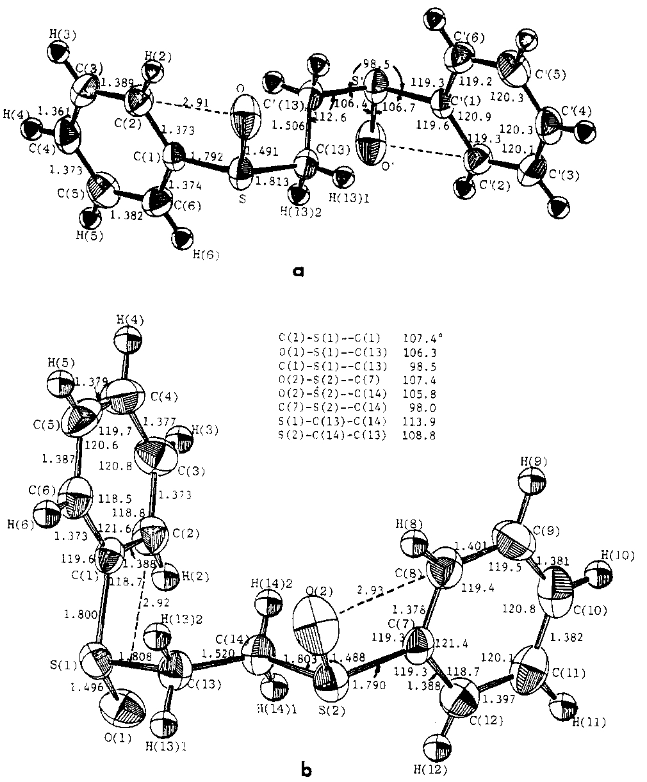


Figure 1. Structures of 1,4-diphenyl-1,4-dithiabutane 1,4-dioxides (**3**) and their bond lengths and angles: (a) meso isomer; (b) *dl* isomer. The root mean square standard deviations of the bond lengths are 0.004 and 0.007 Å for the meso and *dl* isomers, respectively. The root mean square standard deviations of the bond angles are 0.02 and 0.05° for the meso and *dl* isomers, respectively.

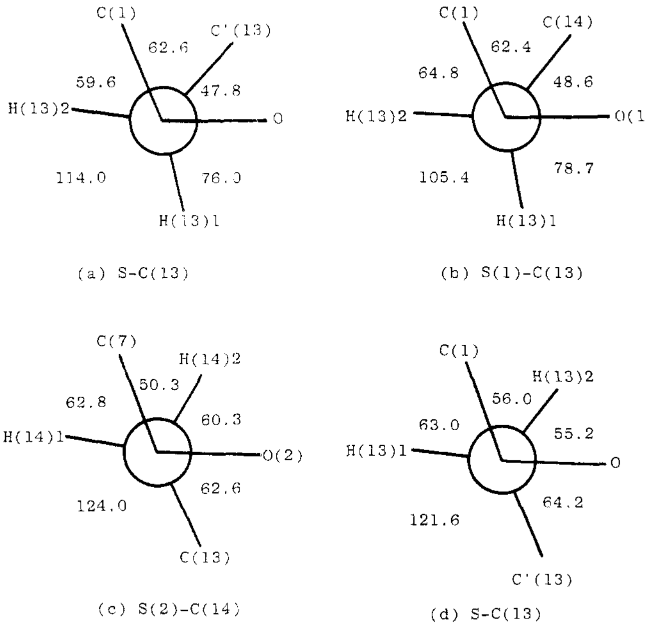


Figure 2. Torsional angles about S–C(sp^3): (a) *meso*-**3**; (b and c) *dl*-**3**; (d) *meso*-**1**.[7]

deviations, are also shown in Figure 1. The mean value of the S–C(sp^2) bond length is 1.796 ± 0.004 Å and that of the S–C(sp^3) bond length is 1.809 ± 0.004 Å. The mean value of the S–O bond length is 1.492 ± 0.003 Å. The mean values of the O–S–C and C–S–C bond angles are 107.6 ± 0.2 and 98.4 ± 0.2°, respectively. These values are in agreement with other sulfoxide structures.[10–12] We are not able to find any features which should demand the unusually high rotational barrier suggested by Taddei.[3b] Indeed, our studies (see below) do not support the existence of an unusually high barrier to rotation in either isomer of **3**.

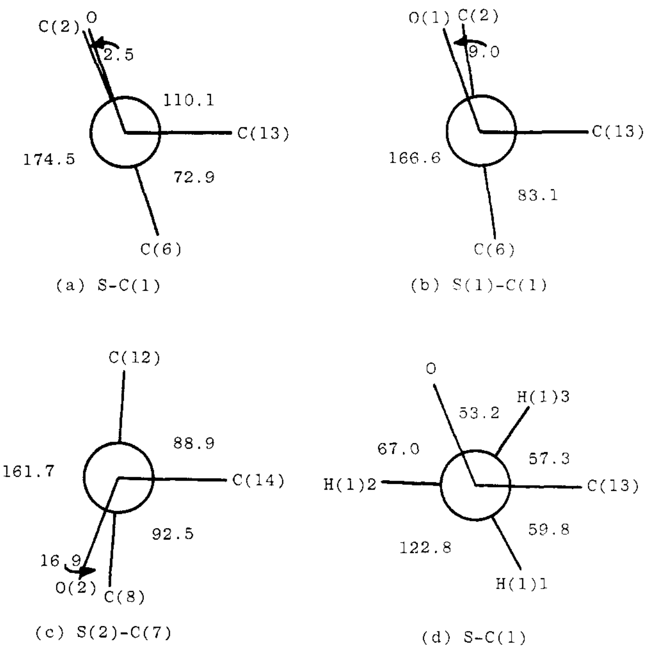


Figure 3. Torsional angles about S–C(sp^2) or S–CH$_3$: (a) *meso*-**3**; (b and c) *dl*-**3**; (d) *meso*-**1**.[7]

The packing of the molecules in the crystal is determined by the van der Waals interactions. No intermolecular distances are less than van der Waals separation. The closest intermolecular contacts between O and C(4)[13] and O and C(6) are 3.36 and 3.40 Å, respectively, in *meso*-**3**, and those between O(1) and C(11), O(1) and C(12), O(1) and C(13), and O(2) and C(4) are 3.47, 3.37, 3.43, and 3.46 Å, respectively, in *dl*-**3**.

Configurational Assignments. Configurations (meso vs. *dl*) already have been assigned to some of the compounds employed in this study[3,6,7] and are set down in unequivocal fashion by the x-ray results just described. Several compounds (e.g., 1,4-dibenzyl-1,4-dithiabutane 1,4-dioxides, **7**) used in this study, while prepared in diastereomeric forms, were not assigned configurations since both isomers exhibited the anticipated[4] (AA'BB') NMR spectra in the ethano region.[14] Several pairs of diastereomers [*meso*- and *dl*-1,4-bis(2-naphthyl)-1,4-dithiabutane 1,4-dioxide (**8**); *meso*- and *dl*-1,4-bis(2-isopropylphenyl)-1,4-dithiabutane 1,4-dioxide (**9**); *meso*- and *dl*-1,4-bis(2-methylphenyl)-1,4-dithiabutane 1,4-dioxide (**10**); *meso*- and *dl*-1,4-bis(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide (**4**); *erythro*- and *threo*-1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide (**11**)] were prepared and configurations assigned by examination of NMR spectra and assuming that the isomer exhibiting the singlet in the ethano region was the meso (or erythro) isomer. (This assumption is consistent with all of the existing literature and with the results presented here.)

In addition, *d*-peroxycamphoric acid was used to prepare optically active (but not optically pure) β-1,4-bis(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide (mp 127–130 °C) (from 1,4-bis(4-methylphenyl)-1,4-dithiabutane), indicating this to be the *dl* form, a conclusion also reached by examination of the ^{1}H NMR spectrum of this material. However, the optical yields (see Experimental Section) are much poorer than those obtained by Mislow.[6]

Configurations were assigned to *meso*- and *dl*-1,4-bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-dioxide (**12**) based upon the ability to partially resolve one isomer (mp 201–202 °C) with *l*-cinchonidine. Chemical correlation, using these carboxylic acids, led to the assignment of configuration to the isomers of 1,4-bis(2-carbomethoxyphenyl)-1,4-dithiabutane

Table I. Proton Chemical Shift Data (δ) for $RS(O)CH_2CH_2S(O)R$[a]

Registry no.	Compd	R	Isomer	CH_2CH_2	Aryl substituent	ArH
21461-90-5	**3**	Phenyl	Meso	3.07[b]		7.45
21461-71-2			*dl*	3.08[c]		7.50
21884-52-6	**4**	4-Methylphenyl	Meso	3.02[b]	2.42	6.99, 7.17, 7.18, 7.33
21884-51-5			*dl*	3.03[c]	2.29	7.28, 7.35, 7.40, 7.48
65311-01-5	**8**	2-Naphthyl	Meso	3.17[b]		7.30–8.10
65311-02-6			*dl*	3.19[c]		7.30–8.10
65378-54-3	**9**	2-Isopropylphenyl	Meso	3.10[b]	1.21, 1.24, 1.28, 1.30[d]	7.30–7.50, 7.78–7.90
65379-00-2			*dl*	3.11[c,e]	*f*	*f*
21884-54-8	**10**	2-Methylphenyl	Meso	3.08[b]	2.35	7.18–7.53, 7.79–7.92
21884-53-7			*dl*	3.07[c]	2.27	7.11–7.44, 7.64–7.84
65311-03-7	**12**	2-Carboxyphenyl	Meso	3.14[b]		7.70–7.98[g]
65311-04-8			*dl*	3.16[c]		7.70–7.98[g]

[a] In $CDCl_3$ at 32 °C unless otherwise specified. Chemical shifts are measured downfield from internal Me_4Si. [b] Singlet. [c] Center of multiplet. [d] CH_3. The methine proton was a multiplet centered near δ 3.08. [e] Estimated from data obtained from a mixture of oxides. [f] Exact values could not be determined from the spectra of a mixture of the oxides. [g] In Me_2SO-d_6.

1,4-dioxide (**13**). The isomer melting at 174 °C was assigned the meso configuration. The NMR criterion was not reliable for assigning configurations to the isomers of **13** since, as described below, both isomers are capable of displaying multiplets for the ethano protons. This appears to be the first example where both *meso*- and *dl*-1,4-diaryl-1,4-dithiabutane 1,4-dioxides may exhibit complex signals for their ethano protons.[15]

Nuclear Magnetic Resonance Spectra. In general, diastereomers prepared in this study can be categorized as having either a singlet or a multiplet for the enthano protons. One of each isomer (meso) of the following showed a singlet (see Table I) in deuteriochloroform at room temperature: **3**, **4**, **8–10**, and **12**. The *dl* isomer of each of the above exhibited the complex symmetric AA′BB′ spectrum expected[4] from an ethano group flanked by two identically substituted chiral centers. The chemical shift of the center of this multiplet corresponded quite closely to the chemical shift of the singlet shown in the corresponding meso form.

To demonstrate that the mere presence of an aryl substituent will not necessarily lead to an A_4 pattern for one stereoisomer, we examined the NMR spectra of *meso*- and *dl*-**7**. Both stereoisomers exhibited a complex AA′BB′ pattern for the ethano protons, similar to what has been reported for the isomers of **1** and **2**.[3a] Of course, this further extends the distinction between aryl and alkyl systems of this type.

To determine whether this degeneracy could be extended to modestly perturbed erythro/threo pairs, we prepared and examined the spectra of the isomers of the 1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide (**11**). One isomer, mp 145.5 °C, was found to exhibit a singlet for the ethano protons, while the other, mp 102 °C, was found to exhibit an AA′BB′ pattern. The singlet had the same band width at half-height as that to the meso isomers, and based upon this parallel pattern we have assigned this isomer the erythro structure.

While it is impossible to computer analyze the A_4 spectra, we have analyzed the AA′BB′ patterns for the *dl* forms of **3**, **4**, **10**, **12**, and **13**. These data, which include several variations in solvent and temperature, are summarized in Table II. In every example, calculated NMR parameters were used to satisfactorily computer simulate the original spectrum.

The temperature dependence of the NMR spectra of the isomers of **3** was determined over the range of −90 to +110 °C. Over this range the ethano singlet of the meso isomer did not become a multiplet and the multiplet of the *dl* isomer did not become a singlet. Indeed, surprisingly little change was observed in the spectrum of the *dl* isomer (suggesting that an intramolecular self-associated form of the disulfoxide is not important over this temperature range). This suggests that the barriers to bond rotation in aryl sulfoxides of this type are, in contrast to the conclusion reached by Taddei,[3b] not excessively high. The chemical shift differences (Δδ) of the A and B protons of several of these compounds as a function of temperature are presented in Table III. While some temperature dependence is evident, it is clear that no compound in this group was on the verge of going from the AA′BB′ to the A_4 pattern.

Raban[17] has discussed the role of "intrinsic nonequivalence" and "conformational preference" in determining the magnitude of magnetic nonequivalence of two like groups proximal to a chiral center. In principle, one should be able to determine the significance of these factors if one can examine spectra at some temperature where the populations are equal.[18] Unfortunately, at the highest temperatures attainable (without decomposition becoming significant; 90–110 °C, *o*-dichlorobenzene solvent) the calculated NMR parameters still were changing. Roberts and co-workers[19] have studied

Table II. ^1H NMR Parameters for the Ethano Multiplets of *dl*-$RS(O)CH_2CH_2S(O)R$[a]

Compd	R	RMS error[d]	δ_A ($\delta_{A'}$)	δ_B ($\delta_{B'}$)	J_{gem}	J_{trans}	J_{gauche}	Temp, °C
3	Phenyl	0.147	340.168	274.257	−13.653	11.140	4.890	+30
		0.066	331.909	269.669	−13.118	10.732	4.995	+58
		0.300	338.482	273.068	−12.857	11.990	4.285	−58
4	4-Methylphenyl	0.132	327.740	268.527	−13.515	10.901	4.859	+30
		0.114	321.857	265.676	−13.470	10.625	5.018	+58
		0.120	326.761	264.123	−13.516	11.007	4.749	+30[b]
10	2-Methylphenyl	0.100	342.231	270.923	−13.347	10.583	5.063	+30
		0.150	337.105	269.029	−13.408	10.298	5.217	+58
12	2-Carboxyphenyl	0.187	360.918	266.099	−12.934	11.602	4.872	+30[c]
13	2-Carbomethoxyphenyl	0.171	378.113	287.704	−13.459	11.727	4.865	+30
		0.151	372.558	285.396	−13.049	11.433	4.828	+58

[a] All J values are given in Hz (taken at 100 MHz). [b] CD_2Cl_2 solvent. [c] Me_2SO-d_6 solvent. [d] RMS, root mean square.

Table III. Nonequivalence of *dl*-$RS(O)CH_2CH_2S(O)R$ Ethano Regions[a]

Compd	R	$\Delta\delta$, Hz	Temp, °C
3	Phenyl	62.2	+58
		65.3	+30
		65.4	−58
4	4-Methylphenyl	51.2	+58
		59.2	+30
		65.1	+90[b]
		70.0	+30[b]
10	2-Methylphenyl	68.1	+58
		71.3	+30
		72.0	−58
13	2-Carbomethoxyphenyl	87.2	+58
		90.4	+30

[a] In $CDCl_3$ unless otherwise specified. Decomposition is observed above +90 °C (in Me_2SO), and the ethano pattern was still changing at the decomposition temperature. [b] *o*-Dichlorobenzene solvent.

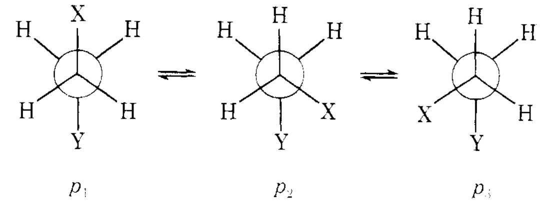
the effect of the substituted 1-phenylpropanes on the nonequivalence of methylene protons. Our results (see Table III) parallel these observations.

The behavior of the higher melting (α)[20] isomer of **13** is exceptional, and to our knowledge this compound represents the first example of a compound of the type $ArS(O)CH_2CH_2S(O)Ar$ in which both stereoisomers exhibit a multiplet for the ethano region.[15] Thus, at 28 °C (deuteriochloroform solvent) both the α and β forms exhibit a multiplet for the ethano protons centered at δ 3.27. (The multiplet for the β form is more complex.) This represents the most noticeable difference in the spectra of the isomers, although the other resonances also differ slightly: δ 3.94 (α-CO_2CH_3) and 3.95 (β-CO_2CH_3); δ 7.50–7.89, 8.07–8.23 (α-ArH) and 7.46–7.90, 8.02–8.25 (β-ArH). However, this difference is unimportant since meso and *dl* isomers which do show the A_4/AA′BB′ disparity also differ in other regions.

The uniqueness of α-**13** is underscored by the temperature and solvent dependence of its NMR spectrum. Thus, unlike the other compounds described in this manuscript, the ethano group is a *singlet* (deuteriochloroform solvent) from +39 to +58 °C (the highest temperature attainable in this solvent). Below +39 °C (deuteriochloroform solvent) this singlet broadens and expands to a multiplet whose complexity continues to increase, even at −58 °C (the lowest temperature attainable in this solvent). This temperature dependency has not been observed in three other solvents. Thus, the ethano region remained a singlet in each of the following solvents at the temperatures shown: CH_2Cl_2, +28, −58, and −94 °C; C_6D_6, +58, +28, and +10 °C; CD_3CO_2D, +80, +28, and +15 °C. Whatever the cause of the collapse of the singlet in $CDCl_3$, it clearly is a function of an interaction of the solvent with the carbomethoxy (and the sulfinyl) group.

We conclude, therefore, that the observation of a multiplet for the ethano protons of compounds of the type $ArS(O)CH_2CH_2S(O)Ar$ can no longer be taken, a priori, as proof of the *dl* (or threo) configuration.

Conformational Analysis by NMR Spectroscopy. It is possible to use the chemical shifts and coupling constants calculated from the NMR spectra to estimate the conformational distribution around the ethano linkage by applying the method of Jung and Bothner-By.[21] We assume the population to be composed of three conformers, present in the mole fractions p_1, p_2, and p_3. In this system $p_2 = p_3 = (1 - p_1)/2$. One can develop the following equation for the *dl* isomer.



$$p_1 = J_{AB} - J_g/J_t - J_g = \frac{(J_t + J_g - J_{AA'} - J_{BB'})}{J_t - J_g}$$

Jung and Bothner-By[21] analyzed the vicinal coupling constants of 64 compounds of known geometry or rotomeric distribution and arrived at "standard" values of J_g (4.10 Hz) and J_t (13.20 Hz). The validity of using this approach for calculations of rotomeric distribution can be established via the additivity relationship developed for the *dl* isomer: $2J_g + J_t$ was found[21] to be 21.30 Hz. The average value for $2J_g + J_t$ found in this study is close to this at 20.86 Hz.

Using this general method we have calculated the rotomeric distribution for **3**, **4**, **10**, **12**, and **13**. These calculations (see Table IV) indicate that at 30 °C the anti conformer predominates, p_1 being about 0.75. The NMR spectra indicate an increasing concentration of the anti conformer as the temperature is lowered. Thus, for *dl*-**3** the mole fraction of anti conformer increases from 0.74 to 0.77 to 0.87 in going from +58 to +30 to −58 °C. This clearly indicates that intramolecular self-association between sulfinyl dipoles (S–O···S–O) is not important in these systems since such attractive interactions are impossible in the anti conformer. This then not only supports the conclusion based upon the CD studies,[6] that intramolecular self-association is unimportant at room temperature,[3a] but also extends this idea to well below room temperature.

Dipole Moment Studies. One can employ the Higasi method,[22] as modified by Krishna and Sirvastava[23] and Altona,[24] to calculate the molecular dipole moments of these sulfoxides. The validity of this approach was confirmed by determining the dipole moments of dimethyl sulfoxide and diphenyl sulfoxide and noting the agreement with literature values.[25,26]

The dipole moments of the isomers of **3**, **4**, **10**, **11**, and **13** were determined in benzene (Table V). It is clear from the data that the α (i.e., meso) and β (i.e., *dl*) diastereomers can be reliably distinguished by dipole moment determinations, with the meso isomers having the lower dipole moment.[27] The data for *erythro*- and *threo*-**11** follows a similar pattern (Table V). Where ortho substituents are absent from the benzene rings, the diastereomers differ in dipole moment by about 1 D.

These dipole moments argue effectively against either diastereomer existing predominantly in solution in a confor-

Table IV. Conformer Distribution in *dl*-$RS(O)CH_2CH_2S(O)R$[a]

Compd	R	p_1[b]	Temp, °C
3	Phenyl	0.74	+58
		0.77	+30
		0.87	−58
		0.73	+30[c]
4	4-Methylphenyl	0.72	+58
		0.75	+30
		0.76	+30[d]
10	2-Methylphenyl	0.68	+58
		0.70	+30
12	2-Carboxyphenyl	0.83	+30[e]
13	2-Carbomethoxyphenyl	0.80	+58
		0.83	+30

[a] In deuteriochloroform unless otherwise specified. [b] Mole fraction of anti conformer. [c] In C_6D_6. [d] In CD_2Cl_2. [e] In Me_2SO-d_6.

Table V. Molecular Dipole Moments of $RS(O)CH_2CH_2S(O)R$

Compd	Isomer	μ,[a] D
3	Meso	3.28
	dl	4.25
4	Meso	3.65
	dl	4.61
10	Meso	3.68
	dl	4.07
11	Erythro	3.50
	Threo	4.59
13	Meso	4.00
	dl	6.20

[a] Benzene solvent. Values are an average of at least three determinations carried out at 20.5 °C.

mation possessing a center of symmetry, in spite of earlier claims to the contrary.[3b]

Experimental Section

1,4-Diphenyl-1,4-dithiabutane.[2] Thiophenol (78 g, 0.71 mol) was reacted with 28 g (0.50 mol) of potassium hydroxide in 400 mL of 95% ethanol. To this was added 64 g (0.34 mol) of 1,2-dibromoethane in 50 mL of 95% ethanol, and the resulting solution was refluxed for 1.5 h. Removal of the solvent, trituration of the residue with water (300 mL), and two recrystallizations of the resultant solid with 95% ethanol afforded 77 g (0.31 mol, 91% yield) of 1,4-diphenyl-1,4-dithiabutane, mp 68–70 °C (lit.[2] mp 69 °C). The NMR spectrum ($CDCl_3$) exhibited a singlet for the ethano protons (δ 3.05, 4 H) and broad singlet phenyl absorption (δ 7.25, 10 H).

***meso-* and *dl*-1,4-Diphenyl-1,4-dithiabutane 1,4-Dioxides (3).** A solution of 28 g of a 30% solution of hydrogen peroxide (0.24 mol) in acetic acid (50 mL) was added dropwise to a stirred solution of 30 g (0.12 mol) of 1,4-diphenyl-1,4-dithiabutane in 200 mL of acetic acid. After stirring for 18 h at 20 °C, the mixture was poured onto 500 mL of ice. The pH was adjusted (sodium hydroxide) to 8, and the resulting precipitate was removed by filtration. Drying (reduced pressure over KOH) afforded 26 g (0.094 mol, 78%) of a crude mixture of isomeric disulfoxides (melting range 125–155 °C).[28]

A mixture of the isomers (5.0 g, 0.018 mol) was recrystallized three times from benzene to afford 1.5 g of the (higher melting) α-1,4-diphenyl-1,4-dithiabutane 1,4-dioxide, mp 164–165 °C (lit.[2] mp 164–165 °C). The mother liquor from the first recrystallization was taken to dryness, and the residue was recrystallized four times from benzene to afford 0.80 g of the (lower melting) β-1,4-dithiabutane 1,4-dioxide, mp 121.5–122.5 °C (lit.[2] mp 121–122 °C).

1,4-Bis(4-methylphenyl)-1,4-dithiabutane. This compound was prepared by reacting *p*-toluenethiol with 1,2-dibromoethane following the procedure described for the synthesis of 1,4-diphenyl-1,4-dithiabutane. The product was obtained in an 80% yield, mp 78.5 °C (lit.[2] mp 81 °C).

***meso-* and *dl*-1,4-Bis(4-methylphenyl)-1,4-dithiabutane 1,4-Dioxides (4).** The starting sulfide was oxidized as described in the preparation of 1,4-diphenyl-1,4-dithiabutane 1,4-dioxide to afford an 85% yield of crude disulfoxide, melting range 127–157 °C. The mixture of sulfoxides (5.0 g, 0.016 mol) was recrystallized four times from benzene to afford 2.0 g of α-1,4-bis(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide, mp 172–173 °C (lit.[2] mp 171–172 °C).

The mother liquor from the first recrystallization was evaporated to two-thirds its original volume, and the resulting precipitate (impure α isomer) was removed by filtration. The filtrate was taken to dryness and the residue recrystallized four times from benzene to afford 1.1 g of β-1,4-bis(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide, mp 129–131 °C (lit.[2] mp 127 °C).

Both isomers were homogeneous by TLC (3:1 v/v chloroform–ethyl acetate eluent, iodine visualization) and isomerically pure by NMR spectroscopy.

1,4-Bis(2-methylphenyl)-1,4-dithiabutane. This compound was prepared by reacting *o*-toluenethiol with 1,2-dibromoethane following the procedure outlined for 1,4-diphenyl-1,4-dithiabutane. The crude product (an oily solid) was recrystallized from *n*-hexane cooled to −78 °C to afford 16.0 g (70%) of 1,4-bis(2-methylphenyl)-1,4-dithiabutane, mp 40–42 °C. The sample was homogeneous by TLC (chloroform eluent, iodine visualization): NMR ($CDCl_2$) δ 2.35 (s, 3 H, CH_3), 3.03 (s, 4 H, CH_2), 7.14 (m, 8 H, C_6H_5).

***meso-* and *dl*-1,4-Bis(2-methylphenyl)-1,4-dithiabutane 1,4-Dioxides (10).** A solution of 8.27 g of 30% hydrogen peroxide (0.073 mol) in 20 mL of acetic acid was added dropwise to a solution of 1,4-bis(2-methylphenyl)-1,4-dithiabutane (10.0 g, 0.o327 mol) in 150 mL of acetic acid. The mixture was stirred overnight at 20 °C and then diluted with an equal volume of ice water and taken to pH 8 (sodium hydroxide). The resulting solid (6.20 g), mp 100–107 °C, was removed by filtration and recrystallized three times from 50% ethanol to afford 5.70 g (0.0186 mol, 57%) of α-1,4-bis(2-methylphenyl)-1,4-dithiabutane 1,4-dioxide, mp 144–146 °C. This material was homogeneous by TLC (3:1 chloroform–ethyl acetate, iodine visualization).

Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.71; H, 5.92. Found: C, 62.88; H, 5.83.

The alkaline filtrate (see above) was extracted with chloroform (4 × 50 mL), and the extract was dried (Na_2SO_4) and concentrated to afford 3.05 g of an oil. This oil was dissolved in 100 mL of warm 1:5 (v/v) benzene–hexane, and the solution was cooled to 0 °C. There resulted 3.30 g of solid, mp 92–95 °C. Two recrystallizations (95% ethanol) yielded 2.70 g (8.82 mmol, 27%) of β-1,4-bis(2-methylphenyl)-1,4-dithiabutane 1,4-dioxide, mp 98–100 °C.

Anal. Found: C, 62.90; H, 6.11.

1-Phenyl-4-(4-methylphenyl)-1,4-dithiabutane. A solution of 2-chloroethylphenyl sulfide (50 g, 0.29 mol) in 180 mL of 95% ethanol was added dropwise (over 30 min) to a stirred solution of *p*-toluenethiol (40 g, 0.32 mol) and potassium hydroxide (18 g, 0.32 mol) in 330 mL of 95% ethanol. The reaction mixture was refluxed gently (2 h), and the solvent was then removed under reduced pressure. The residue (80 g) was washed with water (3 × 100 mL) and then recrystallized twice from 95% ethanol to afford 62 g (0.24 mol, 83%) of 1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane, mp 50.5–51.5 °C. The sample was homogeneous by TLC (3:1 chloroform–ethyl acetate) and had an NMR spectrum ($CDCl_3$) consistent with the structure: δ 2.28 (s, 3 H, CH_3), 3.02 (s, 4 H, CH_2CH_2), 7.03–7.38 (m, 9 H, ArH).

***erythro-* and *threo*-1-Phenyl-4-(4-methylphenyl)-1,4-dithiabutane 1,4-Dioxides (11).** A solution of 55 g of 30% hydrogen peroxide (0.49 mol) in 150 mL of acetic acid was added to a cold (ca. 10 °C) stirred solution of 1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane (58 g, 0.22 mol) in 1.2 L of acetic acid. The reaction mixture was stirred for 24 h, and the solvent was removed under reduced pressure. The residue was dissolved in chloroform (300 mL), and the resulting solution was washed with water (until extracts were neutral) and then with a saturated solution of sodium bicarbonate and finally dried (Na_2SO_4). The solvent was removed to afford 65 g of crude product (mixed isomers), mp 79–122 °C. The mixture exhibited a characteristic[29] S–O stretching mode at 1050 cm^{-1}.

A portion (29 g) of this mixture was recrystallized from ethyl acetate to afford a solid A. The mother liquor B was concentrated (steam bath) to one-half its original volume and allowed to col to afford a solid C. The resulting mother liquor again was treated in this way to afford additional solid D and a mother liquor E. Solids A, C, and D were largely one isomer ("α") based upon the NMR spectra.[30] These three solids were combined and recrystallized twice from ethyl acetate to afford 13 g (0.045 mol, 45%) of α-1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide, mp 144.5–145.5 °C. The sample was homogeneous by TLC (3:1 chloroform–ethyl acetate). The sulfinyl region[29] of the infrared spectrum exhibited two absorptions: 1045 (s) and (s) 1051 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}O_2S_2$: C, 61.61; H, 5.52. Found: C, 61.44; H, 5.44.

Mother liquor E (above) was concentrated (steam bath) to one-fourth its original volume and allowed to cool to room temperature. The resulting solid was separated and recrystallized twice from ethyl acetate to afford 2.3 g (0.0079 mol, 7.9%) of β-1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide, mp 100.5–101.5 °C. This sample was free of the α isomer (NMR) and homogeneous by TLC (3:1 chloroform–ethyl acetate). The sulfinyl region[29] of the infrared spectrum exhibited one absorption at 1048 (s) cm^{-1}.

Anal. Found: C, 61.67; H, 5.59.

***meso-* and *dl*-2,5-Dithiahexane 2,5-Dioxides.**[31] A solution of 2,5-dithiahexane (50 g, 0.41 mol) in acetic acid (400 mL) was mixed with 94 g of 30% hydrogen peroxide (0.38 mol) in 100 mL of acetic acid. After stirring the mixture for 24 h (25 °C) the acetic acid was removed under reduced pressure. The residue was dissolved in refluxing 95% ethanol, and the solution was allowed to cool (slowly) to room temperature. The resulting precipitate was recrystallized six times (95% ethanol) to yield 10 g (0.065 mol, 16%) of α-2,5-dithiahexane 2,5-dioxide, mp 167–168 °C (lit.[31] mp 163–164 °C).

The mother liquor from the first recrystallization was taken to dryness, and the residue was extracted with 200 mL of hot 95% ethanol. The extract was allowed to cool (slowly) to room temperature, and the resulting precipitate was again extracted with hot 95% ethanol. Upon cooling, this extract afforded 12 g of solid, mp 118–126 °C. Three recrystallizations (95% ethanol) afforded 5.6 g (0.036 mol, 8.9%) of β-2,5-dithiahexane 2,5-dioxide, mp 129–130.5 °C (lit.[31] mp 128–130 °C).

***cis-* and *trans-*1,4-Dithiane 1,4-Dioxides.** A solution of 1,4-dithiane (30 g, 0.25 mol) in 500 mL of acetic acid was mixed with 52 g of 30% hydrogen peroxide (0.46 mol) in 100 mL of acetic acid. After stirring for 14 h at 20 °C the solvent was removed under reduced pressure to afford 39 g of a solid residue which was recrystallized from 95% ethanol. The resulting precipitate was recrystallized twice from 95% ethanol and then three times from 50% ethanol to afford 1.5 g (9.9 mmol, 3.9%) of β-1,4-dithiane 1,4-dioxide, mp 250–251.5 °C (lit. 232–235[31] and 250–251 °C[32]).

The mother liquor from the original recrystallization was concentrated to two-thirds its original volume and the precipitate isolated. This was repreated three times, and the final mother liquor was taken to dryness. The residue was recrystallized three times from 50% ethanol to afford 1.6 g (10.5 mmol, 4.2%) of α-1,4-dithiane 1,4-dioxide, mp 283–285 °C dec.[32]

1,4-Dibenzyl-1,4-dithiabutane. A solution of 1,2-dibromoethane (47 g, 0.25 mol) in 50 mL of 95% ethanol was added to a mixture of benzyl mercaptan (62 g, 0.50 mol) and potassium hydroxide (29 g, 0.50 mol) in 500 mL of 95% ethanol. After stirring for 24 h the resulting precipitate (NaBr) was removed, and the filtrate was concentrated to an oil. Distillation of this oil afforded 52 g (0.19 mol, 76%) of 1,4-dibenzyl-1,4-dithiabutane, bp 191–193 °C at 1.6 Torr. Upon standing, this solidified to a pink solid, mp 37–39 °C (lit.[33] mp 38 °C). The NMR spectrum exhibited the anticipated absorptions: δ 2.52 (s, 4 H, CH_2CH_2), 3.65 (s, 4 H, $ArCH_2$), 7.25 (s, 10 H, ArH).

***meso-* and *dl-*1,4-Dibenzyl-1,4-dithiabutane 1,4-Dioxides (7).** A solution of 8.2 g of 30% hydrogen peroxide (0.072 mol) in 10 mL of acetic acid was added to 10 g (0.037 mol) of 1,4-dibenzyl-1,4-dithiabutane dissolved in acetic acid (240 mL). After being stirred overnight, dilution with water afforded 9.5 g (0.034 mol, 92%) of a solid crude mixture of sulfoxides, mp 190–196 °C. The NMR spectrum ($CDCl_3$) of this exhibited a multiplet in the ethano region (δ 2.70–3.30, 4 H), a singlet methylene (δ 4.04, 4 H), and a multiplet aryl resonance (δ 7.20–7.45, 10 H).

A portion (4.6 g, 0.015 mol) of the mixed oxides was extracted with 200 mL of boiling 95% ethanol. The extract deposited 2.6 g of solid (mp 192–196 °C) upon cooling. Three recrystallizations (95% ethanol) afforded 2.0 g (6.5 mmol, 43%) of β-1,4-dibenzyl-1,4-dithiabutane 1,4-dioxide, mp 192–193.5 °C (lit.[33] mp 192–193 °C). The sulfoxide region[29] of the infrared spectrum exhibited strong absorptions at 1090 and 1020 cm^{-1}.

The residue from the original (hot) extraction was recrystallized three times from 95% ethanol to afford 270 mg (0.89 mmol, 6%) of α-1,4-dibenzyl-1,4-dithiabutane 1,4-dioxide, mp 207.5–208 °C (lit.[33] mp 207–208 °C). The sulfoxide region[29] of the infrared spectrum exhibited strong absorptions at 1080, 1028, and 1019 cm^{-1}.

Both α and β isomers were homogeneous by TLC (3:1 v/v chloroform–ethyl acetate).

Asymmetric Oxidation of 1,4-Bis(4-methylphenyl)-1,4-dithiabutane. A solution of *d*-peroxycamphoric acid[34] was added dropwise to a cold stirred solution of 1,4-bis(4-methylphenyl)-1,4-dithiabutane (0.83 g, 3.0 mmol) in 50 mL of chloroform. The resulting solution was stirred (0–5 °C) for 24 h, warmed to room temperature, and washed with saturated sodium bicarbonate solution (3 × 25 mL). Drying (Na_2SO_4) followed by solvent evaporation (N_2 steam) afforded 0.70 g of solid, mp 115–170 °C. TLC (3:1 chloroform–ethyl acetate) indicated the presence of disulfoxides, starting sulfide, and monosulfoxide. The solid was optically active, $[\alpha]^{25}{}_D$ +8.20° (*c* 2.346, chloroform).

This mixture was chromatographed on silica gel (18 g, 60–200 mesh, Brinkman, Brockman activity I; 1.25 × 15.0 cm column) using a 3:1 chloroform–ethyl acetate eluent. This procedure afforded three fractions: starting material (0.20 g); 1,4-bis(4-methylphenyl)-1,4-dithiabutane 1-oxide (0.25 g); and a mixture of disulfoxides (0.20 g), mp 142–155 °C. The last fraction was recrystallized three times from benzene to afford 0.035 g (0.011 mmol) of α-1,4-bis(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide: mp 172–173 °C (lit.[2] mp 172–173 °C); $[\alpha]^{25}{}_D$ 0.00° (*c* 1.75, chloroform).

The mother liquor from the initial benzene recrystallization was taken to dryness, and the residue was recrystallized twice from benzene to afford 0.070 g (0.23 mmol, 35%) of β-1,4-bis(4-methylphenyl)-1,4-dithiabutane 1,4-dioxide: mp 127–130 °C (lit.[2] mp 129–130 °C); $[\alpha]^{25}{}_D$ + 17.9° (*c* 2.935, chloroform). NMR spectroscopy ($CDCl_3$) indicated the absence of the α isomer.

The reaction was repeated twice to afford, in each process, the optically active β isomer: $[\alpha]^{25}{}_D$ +6.67 (*c* 3.24, chloroform) and +180° (*c* 2.39, chloroform).

Methyl *o*-Mercaptobenzoate. This compound was prepared according to the procedure of Katz et al.[35] in 55% yield, bp 98–99 °C (1.75 Torr) [lit.[35] bp 99–100 °C (2.0 Torr)].

1,4-Bis(2-carbomethoxyphenyl)-1,4-dithiabutane. A slurry of sodium hydride (55.8%) in mineral oil (7.70 g slurry, 0.179 mol) was added in small portions to a solution of 30 g (0.179 mol) of methyl *o*-mercaptobenzoate in 500 mL of dry methanol. A solution of 1,2-dibromoethane (16.8 g, 0.0894 mol) in 50 mL of methanol was added dropwise to the yellow thiolate solution. The solution was refluxed until the yellow color disappeared and then cooled. The resulting solid was removed and recrystallized twice from ethyl acetate to afford 29.0 g (0.080 mol, 90%) of 1,4-bis(2-carbomethoxyphenyl)-1,4-dithiabutane, mp 168–169.5 °C. This diester was homogeneous by TLC (3:1 chloroform–ethyl acetate). The NMR spectrum ($CDCl_3$) exhibited signals at δ 2.23 (s, 4 H, ethano), 3.94 (s, 6 H, methyl), and 7.10–7.54 (m, 8 H, ArH).

Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.00; S, 17.69. Found: C, 59.73; H, 4.96; S, 17.47.

1,4-Bis-(2-carboxyphenyl)-1,4-dithiabutane. A mixture of 15 g (0.045 mol) of 1,4-bis(2-carbomethoxyphenyl)-1,4-dithiabutane and 7.0 g (0.12 mol) of potassium hydroxide was refluxed gently for 12 h in 250 mL of a 1:1 (v/v) mixture of methanol–water. The reaction mixture was concentrated to approximately one-half its original volume (reduced pressure) and then acidified (hydrochloric acid) to pH 5. The resulting mixture was filtered to afford 13 g (0.039 mol, 95%) of crude product, mp 294–300 °C. Recrystallization (acetic acid) yielded 11 g (0.033 mol, 80%) of 1,4-bis(2-carboxyphenyl)-1,4-dithiabutane, mp 298–301 °C. This material was homogeneous by TLC (3:1 chloroform-ethyl acetate *and* methanol). The NMR spectrum (Me_2SO-d_6) exhibited absorptions at δ 3.24 (s, 4 H, ethano), 7.70–7.90 (m, 8 H, aromatic), and 12.40–13.50 (s, 1 H, carboxy).

Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.46; H, 4.22; S, 19.18. Found: C, 57.25; H, 4.28; S, 19.33.

***meso-* and *dl-*1,4-Bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-Dioxides (12).** 1,4-Bis(2-carboxyphenyl)-1,4-dithiabutane (22 g, 0.066 mol) was dissolved in 600 mL of water containing 7.3 g (0.128 mol) of potassium hydroxide. A solution of sodium metaperiodate (21.7 g, 0.13 mol) in 400 mL of water was added dropwise (30 min) to the stirred cold (0–5 °C) solution of sulfide. After 18 h the reaction mixture was acidified to pH 5 and the resulting solid was filtered and recrystallized from hot water to afford 14.7 g of solid, mp 175–185 °C. One recrystallization from 95% ethanol followed by three from 2-propanol afforded 4.6 g (0.013 mol, 21%) of β-1,4-bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-dioxide, mp 201–202 °C. This sample exhibited a strong IR absorption at 1053 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_6S_2$: C, 52.42; H, 3.85; S, 17.51. Found: C, 52.33; H, 3.85; S, 17.37.

The aqueous mother liquor (initial recrystallization) was evaporated to dryness, and the residue was recrystallized three times from methanol to yield 5.36 g (0.016 mol, 24%) of α-1,4-bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-dioxide, mp 221–222 °C. The sample exhibited a strong IR absorption at 1018 cm^{-1}.

Anal. Found: C, 52.38; H, 3.99; S, 17.51.

Resolution of β-1,4-Bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-Dioxide (*dl*-12). A solution of (−)-cinchonidine (0.8220 g, 2.76 mmol) in 95% ethanol (25 mL) was added to a solution of 0.500 g (1.38 mmol) of β-1,4-bis(2-carboxylphenyl)-1,4-dithiabutane 1,4-dioxide in 100 mL of 95% ethanol. Since crystallization could not be induced, the solution was taken to dryness (N_2 stream) and the residue was extracted with 100 mL of boiling benzene. Upon cooling, the extract deposited 0.20 g of solid, mp 177–179 °C. Repetition (twice) afforded an additional 0.25 g of material, mp 170–180 °C. All samples melting between 170 and 180 °C were combined and recrystallized from benzene to afford 0.45 g of a solid, mp 179–181 °C. (Further recrystallization of this led to decomposition of the salt.)

The mother liquor from the final benzene crystallization was taken to dryness (N_2 stream). Two careful recrystallizations of the residue (200 mg), mp 80–100 °C dec, from benzene-hexane (1:1, v/v) afforded 80 mg (0.083 mmol, 6.0%) of a solid, mp 145–147 °C dec.

The optical rotation of the higher melting solid (179–181 °C) was $[\alpha]^{26}{}_D$ −193.5° (*c* 0.7900, Me_2SO), while that of the lower melting solid (mp 80–100 °C) was $[\alpha]^{22}{}_D$ +146° (*c* 0.3700, Me_2SO).

A portion of the levorotatory salt (0.235 g, 0.24 mmol) was hydrolyzed with 5% hydrochloric acid to afford 80 mg of solid, mp 187–193 °C. The NMR spectrum of this material indicated that it was a mixture of ~75% α isomer and ~25% β isomer. Recrystallization of this crude acid (2-propanol) afforded 10 mg of β isomer free of α isomer (NMR): mp 201–203 °C; $[\alpha]^{26}{}_D$ −28.2° (*c* 0.4400, Me_2SO).

To remove any possibility of racemization by the hydrochloric acid, a second sample of the levorotatory salt (160 mg, 0.166 mmol) was hydrolyzed in 10% phosphoric acid. This afforded 30 mg of solid, mp 199–201 °C. This consisted (NMR) of 90% β isomer, $[\alpha]^{26}{}_{\mathrm{D}}$ −288° (*c* 0.7750, Me_2SO).

Hydrolysis of the dextrorotatory salt (100 mg) with 10% phosphoric acid afforded 10 mg of solid: mp 199–203 °C; $[\alpha]^{26}{}_{\mathrm{D}}$ +293° (*c* 0.4300, Me_2SO).

Three other partial resolutions produced samples of the β-disulfoxide with rotations of +250, +225, and +253°.

***meso*- and *dl*-1,4-Bis(2-carbomethoxyphenyl)-1,4-dithiabutane 1,4-Dioxide (13).** A solution of 13.0 g (0.115 mol) of 30% hydrogen peroxide in acetic acid (150 mL) was added dropwise to a stirred solution (0–5 °C) of 1,4-bis(2-carbomethoxyphenyl)-1,4-dithiabutane (20.0 g, 0.0552 mol) in methylene chloride (1.2 L). The reaction mixture was stirred for 48 h and washed with water (3 × 500 mL) and saturated sodium bicarbonate (2 × 250 mL). The organic residue was dried (sodium sulfate) and taken to dryness to afford 21.0 g of solid, melting range 130–170 °C. This mixture of sulfoxides was free of starting material (TLC) and exhibited strong absorptions at 1058 and 1028 cm^{-1}.

The crude product (15.0 g, 0.038 mol) was extracted with 200 mL of hot benzene to afford 2.2 g of residue A, mp 175–179 °C. Upon cooling, the extract deposited 0.2 g of solid B, mp 160–165 °C. The filtered and cooled extract was concentrated to two-thirds its original volume to afford 0.3 g of solid C, mp 155–160 °C. Solids A–C were combined and recrystallized three times from benzene to afford 2.0 g (5.1 mmol, 13%) of α-**13**,[20] mp 173–174 °C.

Anal. Calcd for $C_{18}H_{18}O_6S_2$: C, 54.81; H, 4.60; S, 16.26. Found: C, 55.06; H, 4.69; S, 16.42.

The filtrate from solid C was reduced to one-fourth its original volume (steam bath) and cooled to ambient temperature. The resulting precipitate was recrystallized five times from benzene to afford 2.0 g (5.1 mmol, 13%) of β-**13**,[20] mp 157–158.5 °C.

Anal. Found: C, 54.66; H, 4.75; S, 16.42.

TLC (3:1 chloroform–ethyl acetate) and IR spectroscopy indicated that α-and β-**13** were free of one another. The α isomer exhibited strong absorptions at 1095 and 1028 cm^{-1} while the β isomer exhibited strong absorptions at 1099, 1060, and 1030 cm^{-1} in the sulfoxide region.[29]

Hydrolysis of *meso*- and *dl*-1,4-Bis(2-carbomethoxyphenyl)-1,4-dithiabutane 1,4-Dioxide (13) to *meso*- and *dl*-1,4-Bis(2-carboxyphenyl)-1,4-dithiabutane 1,4-Dioxide (12). A suspension of 1.0 g (2.5 mmol) of α-**13** in a solution of 0.42 g (6.2 mmol) of potassium hydroxide in 1:1 methanol–water (80 mL) was refluxed overnight. Acidification (pH 6) produced a solid which was washed and dried (under vacuum over potassium hydroxide) to afford 0.79 g (2.2 mol, 86%) of crude α-**12**, mp 218–220 °C. Two recrystallizations (methanol) afforded 0.51 g (1.4 mmol) of α-**12**, identical with material prepared by oxidation of the corresponding sulfide.

The isomer β-**13** was hydrolyzed similarly to afford β-**12**, identical with material prepared by oxidation of the corresponding sulfide.

Dipole Moment Determinations. The dielectric constants of solutions of the compounds of interest were determined with a dipolmeter,[36] type DM 01, equipped with DFL-1 cell. The cell was calibrated using methylcyclohexane, cyclohexane, carbon tetrachloride, and benzene, with the dielectric constants taken[37] as 2.0202, 2.0228, 2.2363, and 2.2825, respectively. All determinations were carried out at 20.5 ± 0.1 °C. Unknowns were examined in benzene solutions (concentrations varied from 0.01–0.20 g/25–50 mL). Each sample was examined in no less than three separate determinations. Flow-through cells were used, and they were filled from the bottom in order to avoid air pockets in the cell.

X-ray Analysis. Single crystals of *meso*- and *dl*-**3** were grown from ethanol solutions in the form of clear prisms. The unit cell parameters and intensity data were measured on a Syntex $P\bar{1}$ computer-controlled diffractometer. The crystal data are summarized in Table VI. A θ–2θ scanning mode with graphite monochromatic Mo Kα radiation was used in the intensity measurements. A reflection was considered as being observed if the intensity, I, was greater than twice its standard deviation, $\sigma(I)$, and they were calculated by using the following formulas: $I = S(C - RB)$ and $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, and the parameter p is an instability factor which was set at 0.07. The intensity data were then reduced to structure factors by the application of Lorentz–polarization factors, and no absorption corrections were applied. The observed structure factor, F_o, and its standard deviation, $\sigma(F_o)$, were defined as $|F_o| = [I(Lp)^{-1}]^{1/2}$ and $\sigma(F_o) = [\sigma(I)(Lp)^{-1}]/2|F_o|$, where Lp is the Lorentz–polarization correction.

Table VI. Crystal Data for $C_{14}H_{14}S_2O_2$ (fw 278.39)

	Meso isomer	*dl* isomer
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions	a = 8.327 (1) Å	a = 5.629 (1) Å
	b = 9.395 (2) Å	b = 14.532 (4) Å
	c = 8.974 (2) Å	c = 16.455 (4) Å
	β = 105.34 (1)°	
	V = 677.0 (2) Å^3	V = 1346.0 (2) Å^3
Density calcd	1.366 g/cm^3	1.380 g/cm^3
Density measd (flotation)	1.35 g/cm^3	1.37 g/cm^3
Molecules/unit cell	2	4
Linear absorption coefficient (Mo Kα radiation)	3.75 cm^{-1}	3.78 cm^{-1}
Crystal size	0.28 × 0.30 × 0.31 mm	0.20 × 0.21 × 0.69 mm

Structure Determination. Both structures in Figure 1 were determined by the heavy atom method. The refinements were carried out by the full-matrix least-squares method with isotropic temperature factors and by the block-diagonal least-squares method with anisotropic temperature factors. All of the hydrogen atoms were located on difference Fourier synthesis. The temperature factors of the hydrogen atoms were made the same as those of the atoms to which they are bonded. The weight of the reflection was assigned as $1/\sigma(F_o)^2$. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. The final R index $(\sum||F_o| - |F_c||/\sum|F_o|)$ was 0.037 for the meso isomer and 0.056 for the *dl* isomer. The atomic scattering factors used for sulfur, oxygen, and carbon atoms were those from the "International Tables for X-ray Crystallography",[38] and for hydrogen the values given by Stewart, Davidson, and Simpson[39] were used. The final positional and thermal parameters are given in Table VII (see Supplementary Material paragraph).

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Registry No.—*meso*-**7**, 56348-34-6; *dl*-**7**, 56348-33-5; *erythro*-**11**, 65311-05-9; *threo*-**11**, 65310-90-9; (−)-(R^*,R^*)-**12**, 65310-91-0; (+)-R^*,R^*)-**12**, 65310-93-2; (−)-(R^*,R^*)-**12** cinchonidine salt, 65310-92-1; (+)-(R^*,R^*)-**12** cinchoridine salt, 65310-94-3; *meso*-**13**, 65310-95-4; *dl*-**13**, 65310-96-5; 1,4-diphenyl-1,4-dithiabutane, 622-20-8; thiophenol, 108-98-5; 1,2-dibromoethane, 106-93-4; 1,4-bis(4-methylphenyl)-1,4-dithiabutane, 3238-95-7; *p*-toluenethiol, 106-45-6; 1,4-bis(2-methylphenyl)-1,4-dithiabutane, 65310-97-6; *o*-toluenethiol, 137-06-4; 1-phenyl-4-(4-methylphenyl)-1,4-dithiabutane, 65310-98-7; *meso*-2,5-dithiahexane 1,5-dioxide, 21884-56-0; *dl*-2,5-dithiahexane 2,5-dioxide, 21884-55-9; 2,5-dithiahexane, 6628-18-8; *cis*-1,4-dithiane 1,4-dioxide, 10348-97-7; *trans*-1,4-dithiane 1,4-dioxide, 10348-98-8; 1,4-dithiane, 505-29-3; 1,4-dibenzyl-1,4-dithiabutane, 24794-19-2; benzyl mercaptan, 100-53-8; 1,4-bis(4-methylphenyl)-1,4-dithiabutane 1-oxide, 65310-99-8; 1,4-bis(2-carbomethoxyphenyl)-1,4-dithiabutane, 65311-00-4; methyl *o*-mercaptobenzoate, 4892-02-8; 1,4-bis(2-carboxyphenyl)-1,4-dithiabutane, 52961-83-8; (−)-cinchonidine, 485-71-2.

Supplementary Material Available: Table VII of fractional atomic coordinates and thermal parameters for *meso*- and *dl*-**3** (2 pages). Ordering information is given on any current masthead page.

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(15) We have observed that both *meso*- and *dl*-1,4-dimesityl-1,4-dithiabutane 1,4-dioxides exhibit complex ethano regions under all of the conditions enployed (−20 to +60 °C in CDCl$_3$, C$_6$D$_6$, and C$_5$D$_5$N). The x-ray and NMR studies of these will be discussed in a future communication. Asymmetric synthesis[6] has been used to prepare the enantiomerically enriched (+)-*R,R* diastereomer.[16]
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Ten-Membered Ring Heterocyclic Molecules Containing Phosphorus, Oxygen, and Nitrogen

J. B. Robert*[1a] and H. Weichmann[1b]

Laboratoire de Chimie Organique Physique, E.R.A. No. 674 C.N.R.S., Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, F-38041 Grenoble Cedex, France

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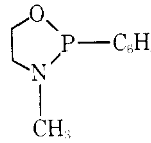
The five-membered ring 2-phenyl-1,3,2-oxazaphospholidine exists in solution in equilibrium with its ten-membered ring dimers and polymeric species of high molecular weight. The corresponding 2-thiono derivatives have been prepared by direct addition of elemental sulfur. The ^{1}H, ^{13}C, and ^{31}P NMR spectral parameters are reported along with a discussion concerning the five-membered ring conformation.

In previous papers we described spontaneous dimerization from various 1,3,2-dioxa and 1,3,2-dithia organophosphorus molecules. Thus, ten-membered rings have been obtained from 2-phenyl-1,3,2-dioxaphospholane,[2a] 12-membered rings from 2-methyl-1,3,2-dioxaphosphorinane[2b] and from 2-*tert*-butyl-1,3,2-dithiaphosphorinane,[3] 14-membered rings from 2-*tert*-butyl-1,3,2-dioxaphosphepane,[4] and 16-membered rings from 2-methyl-1,3,6,2-trioxaphosphocane.[5]

In those reactions, besides dimers one observes the formation of polymeric species which are under investigation and whose structure (cyclic or not cyclic) has not yet been established.

Such a dimerization has not been observed starting from 1,3,2-diazaphospholidines or 1,3,2-diazaphosphorinanes. However, due to the influence of minor experimental factors (moisture, nature of the storing vessel) on the evolution of the reaction when it takes place, we cannot conclude that this reaction does not take place with 1,3-diaza compounds. Thus, it seemed interesting to investigate the behavior of 1,3-oxaza compounds (–O–P–N–). As according to our previous results, the dimerization is more easily observed in dioxaphospholanes than in dioxaphosphorinanes or dioxaphosphepanes, and as this reaction goes easily with the 2-phenyl-1,3,2-dioxaphospholane, the 2-phenyl-1,3,2-oxazaphospholidine 1 appeared to be a good candidate for a possible ring-expansion reaction.


1

Some results have been previously reported on the behavior of 2-substituted 1,3,2-oxazaphospholidines. 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine (1) is an interesting compound, since, at room temperature, it polymerizes into a solid in a reversible reaction. The polymer formula was written as a linear chain [OCH$_2$CH$_2$N(CH$_3$)P(C$_6$H$_5$)–]$_n$.[6] In another study, the 2,3-dimethyl-1,3,2-oxazaphospholidine was said to exist as a dimer but no details concerning the dimer identification or stereochemical discussions were given.[7]