internal reference. Mass spectra were obtained on a JEOL JMS-O1SG-2 spectrometer at 75 eV by using a direct inlet system. Gas chromatographic analyses were carried out by means of a Yanagimoto Yanaco G8 YR-101 (30% high-vacuum silicon grease; 2 m; temperature 110 °C; carrier gas, helium 50 mL/min).

The yields, melting points, appearances, solvents for recrystallizations, elemental analyses, and spectral data of the reaction products are summarized in Tables I–IV (Tables III and IV as supplementary material).

The dienones **1a** and **1b** were prepared by the reported method. Commercial grade pyridines **4a–e** were used without purification. **1a**: pale yellow prisms; mp 78–80 °C (petroleum ether, bp 40–60 °C) (lit.[7,8] mp 80 °C). **1b**: pale yellow needles; mp 94–95 °C (ethanol) (lit.[8] mp 94–95 °C).

Reaction of 1 with Pyridines 4a–e. Typical Procedure. A reaction mixture of **1a** (3.4 g, 10 mmol), pyridine (**4a**; 1.6 g, 20 mmol) and ethylene glycol (EG; 1.1 m, ca. 10 mmol) was heated in an oil bath at 110 °C for 1 h with stirring under a nitrogen stream to form a pale yellow mass with the evolution of isobutylene (**13**), which was carried by the nitrogen into a mixture of dry toluene (50 mL) contained aluminum chloride (0.05 g) which had been purified by sublimation just prior to use, giving *tert*-butyltoluenes (**14**, 25%). The isomer distribution of **14** was determined by gas chromatography to be 7:93 meta/para. The masses were washed with water, hexane, and benzene to give pyridinium bromide (**7a**) as fine colorless needles, which gave a satisfactory elemental analysis without further purification: 45% yield; mp ~300 °C dec. The organic layers were combined and washed with 10% HCl aqueous solution and then water. The organic layer was dried over sodium sulfate and then evaporated in vacuo to leave a residue. The residue was column chromatographed on silica gel (Wako gel C-300) with at first hexane (A), then benzene (B), and finally ethyl acetate (C) as eluants. The compounds **9** and **12** were obtained from fraction A, **11** was isolated from B, and **5** was eluted from fraction C. The IR spectra of known products **5**, **9**, **11**, **12**, and **14** were identical with those of the authentic samples.

Preparation of 8 from 7. Typical Procedure. To the compound **7a** (3.64 g, 10 mmol) in methanol (50 mL) was added aqueous 10% NaOH solution (10 mL) followed by addition of water (ca. 100 mL) to form the precipitate of **8a** as orange yellow needles. The elemental analysis of **8a** indicated that the monohydrate of **8a** ($C_{19}H_{25}NO{\cdot}H_2O$) was orange-red needles and the tetrahydrate orange-yellow needles.

Preparation of 7 from 8. Typical Procedure. To the monohydrate of **8a** (0.3 g, 1 mmol) in methanol (20 mL) was added aqueous 10% HBr solution (ca. 2 mL). The solution was then evaporated in vacuo to give white crystals of **7a**, 0.34 g (ca. 100%).

Sodium Borohydride Reductions of 7 and 8. Typical Procedure. To a solution of **7a** (1 g, 2.74 mmol) in methanol (20 mL) was added $NaBH_4$ (ca. 1.0 g) by portions over a 15-min period at room temperature. After the solution was allowed to stand for 15 min (in the cases of **7c,e** and **8e**, the solutions were refluxed for 3 h), the methanol was evaporated in vacuo to leave a crystalline residue. To the residue was added water (ca. 10 mL), and it was extracted with benzene 3 × 50 mL). The benzene layer was washed with aqueous 10% sodium bicarbonate solution and water. The organic layer was dried over sodium sulfate and evaporated in vacuo to give a residue which gave crude **21a** after washing with cold methanol. Recrystallization from a mixture of methanol and water gave colorless needles, 0.5 g (63% yield).

Catalytic Hydrogenations of 21. Typical Procedure. To a solution of **21a** (2.3 g, 8 mmol) in ethanol (100 mL) was added Raney Ni (W2) in ethanol (10 mL). The reaction mixture was then kept to stand at room temperature with stirring under hydrogen atmosphere. After the reaction was completed, the Raney Ni was taken off by filtration. The filtrate was evaporated in vacuo to leave pale blue crystals of crude **22a**. Recrystallization from a mixture of methanol and water gave pale blue needles, 1.9 g (82% yield).

Reaction of 16 with Pyridine (4a). After a solution of 1 g (3.5 mmol) of **16** in 5 mL of **4a** was refluxed for 1.0 h, the solution was evaporated in vacuo to leave orange-red residue. The residue was extracted with benzene. The benzene solution was washed with water and then dried over sodium sulfate. The organic layer was evaporated in vacuo to give orange-red crystals. Recrystallization of the crystals from methanol gave 0.61 g (85%) of **17** as orange needles, mp 241–243 °C (lit.[15] mp 241–243 °C).

Registry No. **1a**, 1988-75-6; **1b**, 5457-60-3; **4a**, 110-86-1; **4b**, 109-06-8; **4c**, 108-99-6; **4d**, 108-89-4; **4e**, 591-22-0; **5**, 73405-44-4; **6**, 78672-47-6; **7a**, 73405-43-3; **7c**, 78657-01-9; **7e**, 78657-02-0; **7f**, 78657-03-1; **7h**, 78657-04-2; **7i**, 78657-05-3; **7j**, 78657-06-4; **8a**, 35889-95-3; **8c**, 78657-07-5; **8d**, 78657-08-6; **8e**, 78657-09-7; **9**, 732-26-3; **11**, 4971-61-3; **12**, 719-22-2; *m*-**14**, 1075-38-3; *p*-**14**, 98-51-1; **16**, 1139-52-2; **17**, 2455-14-3; **21a**, 73405-45-5; **21b**, 78657-10-0; **21b**·HCl, 78657-11-1; **21c**, 78657-12-2; **21d**, 78657-13-3; **22a**, 78657-14-4; **22b**, 78657-15-5; **22c**, 78657-16-6; **22d**·HCl, 78657-17-7.

Supplementary Material Available: Tables III and IV showing the combustion analytical data and the NMR spectral data for **7a–j**, **8a–e**, **21a–c**, and **22a–d** (3 pages). Ordering information is given on any current masthead page.

Restricted Internal Rotations in Some Ortho-Substituted Diaryl Sulfides and Sulfones

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Restricted rotations about sulfur–aryl bonds were studied by ^1H NMR spectroscopy for a series of 2,6,2′,6′-tetrasubstituted diaryl sulfides (**3–6**) and sulfones (**7–11**) each of which bears at least two 2-hydroxy-2-propyl or 2-alkoxy-2-propyl substituents. Each shows two peaks for diastereotopic geminal methyl groups in its room-temperature NMR spectrum. Coalescence of the two methyl peaks was observed at higher temperature. The differing energy requirements for gear-meshing and gear-clashing modes of synchronous roatations of the two rings are invoked to explain these observations for **3–10**. A ring-inversion mechanism is proposed for **11**. Free energies of activation fall in the range 18.5–24.6 kcal mol^{-1} for the conformational interconversions responsible for the coalescence of the two methyl peaks in these compounds. The chirality of **3**, **5**, and **7** was demonstrated by using Pirkle's chiral alcohol as an NMR solvent.

In the course of our studies in persulfurane chemistry,[1] several diaryl sulfides and sulfones, in which both benzene rings are doubly ortho substituted, have been synthesized and characterized. Some of these highly substituted diaryl

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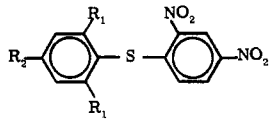
compounds provide interesting NMR evidence for restricted rotations about the sulfur–aryl bonds. An example of related hindered rotations around benzene–sulfur bonds has been reported by Kessler and co-workers[2] on sulfides 1 and 2. Restricted rotations are common for compounds



1 $R_1 = R_2 = CH(CH_3)_2$

2 $R_1 = CH_2CH_3$; $R_2 = H$

containing two or more ortho-substituted aryl rings (Ar) attached to a central atom (Z). Examples for the Ar_2Z systems include diaryl ethers[2,3] as well as the sulfides and sulfones we consider in this paper. Triarylmethanes[4,5a,b] and triarylamines[5c] are examples of Ar_3Z systems which have been studied. We here report ^1H NMR studies of isomerism resulting from restricted rotational modes in some of these sulfides and sulfones.

Experimental Section

General Methods. Proton NMR chemical shifts are reported on the δ scale (parts per million downfield from tetramethylsilane as an internal standard). Melting points were determined on a micro hot stage. Elemental analyses of new compounds are within 0.4% of the theoretical values, unless otherwise noted. Probe temperatures were determined by measuring the temperature-dependent peak separations for methanol (low temperature) and ethylene glycol (high temperature).

Solvent and Reagents. Ether, tetrahydrofuran (THF), and pentane were dried and stored over sodium wire. Chloroform was dried by distillation from P_2O_5.

Bis[2-(1-methoxy-1-methylethyl)-4-(1,1-dimethylethyl)-6-(methoxymethyl)phenyl] Sulfide (6). To a stirred solution of sulfide tetraol **5**[1] (400 mg, 0.84 mmol) and 18-crown-6 ether (0.89 g, 3.36 mmol) in 10 mL of THF was added excess powdered KH (172 mg, 4.2 mmol). After 1 h, excess CH_3I (0.2 mL, 80.3 mmol) was added to the brownish suspension. After 30 min, the solution was filtered, and the solvent was removed to give a semisolid residue, which was redissolved in ether. The ether solution was washed with water and dried (Na_2SO_4), and the solvent was removed to give an oil, which was identified by ^1H NMR as the dimethylated product. The above procedure was repeated with the dimethylated product as the starting material to give the desired product, the tetramethoxy sulfide **6**: 200 mg (0.38 mmol, 45%); mp 119–121 °C; ^1H NMR ($CDCl_3$) δ 7.36 (d, 2, Ar H), 7.27 (d, 2, Ar H), 4.12 and 3.22 (AB pattern, 4, J = 14 Hz, CH_2OCH_3), 3.17 (s, 6, OCH_3), 3.0 (s, 6, OCH_3), 1.94 (s, 6, $OCCH_3$), 1.78 (s, 6, $OCCH_3$), 1.34 (s, 18, $C(CH_3)_3$); mass spectrum (15 eV), m/e (relative intensity) 530 (91.89, M^+·), 498 (36.09, M^+· – CH_3OH), 466 (36.09, M^+· – $2CH_3OH$). Anal. ($C_{32}H_{50}O_4S$) C, H.

General Procedure of Oxidation of Sulfides to Sulfones with *m*-Chloroperbenzoic Acid (MCPBA). A solution of MCPBA (2 equiv) in chloroform was added to a stirred solution of sulfide in chloroform. After a period of time (usually 2–3 h), the solution was washed with aqueous $NaHCO_3$ and dried (Na_2SO_4). Removal of solvent gave the desired product, which was recrystallized from ether–pentane.

Tetraol Sulfone 9. Sulfone **9** was obtained in 75% yield: mp 128.5–130 °C; IR ($CHCl_3$) 3448 (m, OH stretching), 2959 (s), 1600 (m), 1366 (s), 1275 (s), 1155 (s), 1115 (s), 1023 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57 (d, 2, Ar H), 7.46 (d, 2, Ar H), 5.0 (br, 2, OH), 4.47 and 4.01 (AB pattern, 4, J = 14 Hz, CH_2OH), 2.4 (br, 2, OH), 1.81 (s, 6, $OCCH_3$), 1.77 (s, 6, $OCCH_3$), 1.35 (s, 18, $C(CH_3)_3$); mass spectrum (10 eV), m/e (relative intensity) 506 (M^+· not observed), 488 (0.52, M^+· – H_2O), 407 (2.69), 373 (4.07), 253 (10.2), 156 (100); field desorption mass spectrum, m/e (estimated relative intensity) 506 (40), 488 (100). Anal. ($C_{28}H_{42}O_6S$) C, H, S.

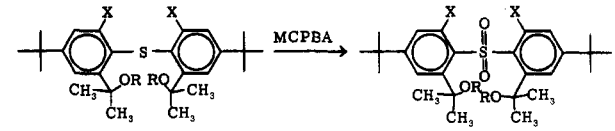
Diester Diol Sulfone 7. Sulfone **7** was obtained in 77.5% yield: mp 213–215 °C; IR ($CHCl_3$) 3413 (m, OH stretching), 2958 (s), 1698 (s), 1595 (m), 1464 (m), 1370 (s), 1312 (s), 1250 (s), 1198 (s), 1124 (s), 1020 (m), 978 (w), 888 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (d, 2, Ar H), 7.10 (d, 2, Ar H), 4.87 (s, 2, OH), 4.38 (q, 4, J = 7.2 Hz, OCH_2CH_3), 1.70 (s, 6, $OCCH_3$), 1.50 (s, 6, $OCCH_3$), 1.36 (t, 6, J = 7.2 Hz, OCH_2CH_3), 1.30 (s, 18, $C(CH_3)_3$); mass spectrum (70 eV), m/e (relative intensity) 574 (0.26, M^+· – O), 557 (5.01, M^+· – O_2H), 545 (5.70), 511 (8.97), 483 (16.57), 405 (24.53); field desorption mass spectrum, m/e (estimated relative intensity) 591 (50), 573 (100). Anal. ($C_{32}H_{46}O_8S$) C, H.

Tetramethoxy Sulfone 10. Sulfone **10** was obtained in 75% yield: mp 120–123 °C; ^1H NMR ($CDCl_3$) δ 7.69 (d, 2, Ar H), 7.36 (d, 2, Ar H), 4.25 and 3.11 (AB pattern, 4, J = 13 Hz, CH_2OCH_3), 3.06 (s, 6, OCH_3), 2.96 (s, 6, OCH_3), 2.01 (s, 6, $OCCH_3$), 1.83 (s, 6, $OCCH_3$), 1.37 (s, 18 $C(CH_3)_3$); mass spectrum (80 eV), m/e (relative intensity) 562 (M^+· not observed), 545 (0.36, M^+· – OH), 531 (0.76, M^+· – CH_3O), 515 (1.25), 483 (1.07), 451 (2.03), 443 (2.50); field desorption mass spectrum, m/e (estimated relative intensity) 562 (67), 530 (100, M^+· – CH_3OH). Anal. ($C_{32}H_{50}O_6S$) C, H.

Bis[2-(1-hydroxy-1-dimethylethyl)-4-(1,1-dimethylethyl)-6-carboxyphenyl] Sulfone (8). Diester sulfone **7** (112.6 mg, 0.19 mmol) in 14 mL of methanol and 8 mL of aqueous KOH (ca. 15%) was boiled for 18 h. The solution was added into dilute HCl to give a white suspension, which was extracted once with $CHCl_3$ and once with ether. Both solvents, however, failed to dissolve all the solid in the aqueous layer. The organic phases, and the insoluble solid, were combined, and the solvent was removed to give a white residue, which was washed with water and air-dried. Recrystallization from acetone–water afforded crystals of **8**: 75 mg (0.14 mmol, 73.7%); mp 242–246 °C; IR (Nujol) 3390–2666 (m), 1715 (s), 1689 (s) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.40 (d, 2, Ar H), 7.15 (d, 2, Ar H), 5.60 (br, 2, OH), 1.60 (s, 6, $OCCH_3$), 1.45 (s, 6, $OCCH_3$), 1.32 (s, 18, $C(CH_3)_3$). Anal. ($C_{28}H_{38}O_8S$) C, H, S.

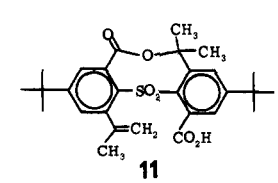
Results

The syntheses of sulfides **3–5** and sulfone lactone **11** have been reported.[1] Sulfides **3**, **5**, and **6** were oxidized by *m*-chloroperbenzoic acid to give the corresponding sulfones **7**, **9**, and **10**. Sulfone diacid **8** was prepared by the saponification of sulfone diester **7** in methanolic KOH solution.



3 X = COOEt; R = H
4 X = COOH; R = H
5 X = CH_2OH; R = H
6 X = CH_2OCH_3; R = CH_3

7 X = COOEt; R = H
8 X = COOH; R = H
9 X = CH_2OH; R = H
10 X = CH_2OCH_3; R = CH_3



11

The observation of two nonequivalent geminal methyl peaks in the room-temperature NMR spectrum is common for these symmetrically substituted sulfides and sulfones (**3–10**). The diastereotopic methylene protons of the ethyl group in sulfide **3** and sulfone **5** give rise to ABX_3 pattern multiplets, and the methylene protons in **5**, **6**, **9**, and **10** show an AB pattern. In the case of sulfides **3** and **5** and

(1) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1659; *ibid.*, in press.
(2) Kessler, H.; Rieker, A.; Rundel, W. *Chem. Commun.* **1968**, 475.
(3) (a) Bergman, J. J.; Chandlwe, W. D. *Can. J. Chem.* **1972**, *50*, 353. (b) Lehmann, P. A. *Org. Magn. Reson.* **1970**, *2*, 467.
(4) Sabacky, M. J.; Johnson, S. M.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1969**, *91*, 7542.
(5) (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3198. (b) Andose, J. D.; Mislow, K. *Ibid.* **1974**, *96*, 2168. (c) Glaser, R.; Blount, J. F.; Mislow, K. *Ibid.* **1980**, *102*, 2777.

Table I. Free Energies of Activation for the Coalescence of the Two Methyl Peaks in Sulfides 3-6 and Sulfones 7-11

compd	solvent	$\Delta\nu$, Hz[a]	T_c, °C[b]	ΔG^*, kcal mol^{-1}
3	Ph_2O	4.3	67.5	18.5
4	Me_2SO-d_6	3.8	87.5	19.7
5	Ph_2O	10.1	117.5	20.6
6	Me_2SO-d_6	15.2	164	22.8
7	Me_2SO-d_6	8.2[e]	163[e]	22.9[f]
8	Me_2SO-d_6	12.8	>145[c]	>22.0[d]
9	Me_2SO-d_6	4.9	142	22.6
10	Me_2SO-d_6	11.9	163[g]	24.6[f]
11	Ph_2O-$CDCl_3$ (5:1 v/v)	7.7	91.5	19.4

[a] $\Delta\nu$ is the separation of the methyl singlets in hertz. [b] T_c is the coalescence temperatures. [c] The highest accessible in this experiment. The two methyl peaks were broadened, but the sample proved too unstable to allow adequate determination of ΔG^* by line-shape analysis. [d] The lower limit of ΔG^*. [e] Near coalescence, measured at 60 MHz. [f] Calculated by line-shape analysis using a modified LAOCOON3 program. See: Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jessop, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 4701. [g] Considerably below T_c, but the highest temperature allowed by the stability of the compound.

sulfone **7**, the upfield methyl peak is resolved into two singlets upon addition of (*R*)-(−)-2,2,2-trifluoro-1-phenylethanol[6] to samples in $CDCl_3$, demonstrating the chirality of the molecules.

The ^1H NMR spectra of **3**–**11** are temperature-dependent in the geminal methyl region. At sufficiently high temperatures magnetic equivalence of the two geminal methyls is observed. From the coalescence temperatures and the chemical shift separations of the two peaks at lower temperature, the free energies of activation (ΔG^*) were calculated by using the Gutowsky–Holm equation.[7] Table I lists the data from high-temperature ^1H NMR studies on the sulfides (**3**–**6**) and the sulfones (**7**–**11**). Complete coalescence of the two methyl peaks in sulfones **7**, **8**, and **10** was not observed at the highest temperatures accessible in these investigations.[8] Values of ΔG^* at lower temperatures were calculated by using line-shape analysis for **7** and **10**. The thermal instability of **8** was such as to prevent the application of the line-shape analytical approach, so we quote only the lower limit of ΔG^* for the process leading to methyl peak coalescence for this compound.

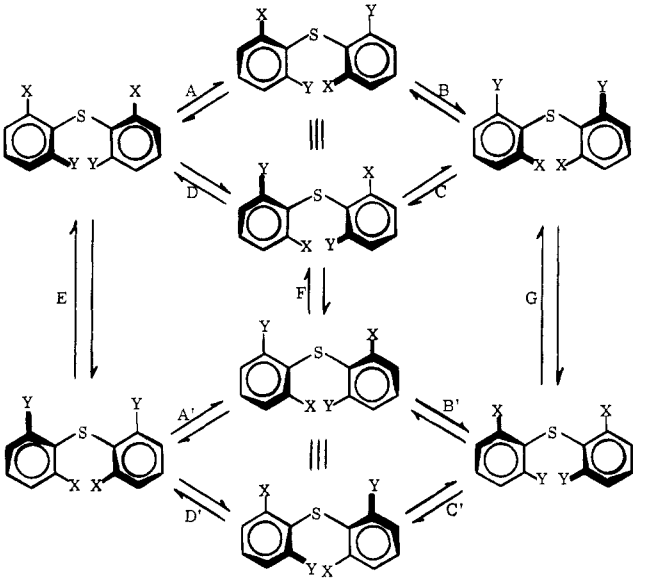
Discussion

Conformational Interconversions in Acyclic Diaryl Sulfides. Kessler, Rieker, and Rundel report[2] the observation of nonequivalence of the *o*-alkyl groups of sulfides **1** and **2** and quote values for the activation barrier ($\Delta G^{\ddagger}$) for their interconversion as 15.1 kcal mol^{-1} at 0 °C. The activation barrier which we have determined for sulfides **3**–**6** (Table I) is larger, probably because of the greater degree of steric hindrance. Both benzene rings are doubly ortho substituted in our compounds. Hydrogen bonding between ortho substituents may also be important in determining conformational rigidity.

The mechanistic aspects of this process in diaryl sulfides and other similar systems such as Ar_2O, Ar_2CH_2, Ar_2CO, and Ar_2PH and triaryl systems like Ar_3CH, Ar_3P, and Ar_3B have been extensively studied and analyzed in depth.[9] Mislow and Gust[9] have presented a detailed analysis of the "ring-flip" mechanisms, as they call them, or "gear meshing–gear clashing" mechanisms, as they are called in our laboratory,[4] for rotations about single bonds such as the C–S bonds in the compounds discussed here. These mechanisms involve no inversion at the central atom, sulfur in the present case, to explain the observations relating to site exchange for the ortho substituents. There are six possible conformations for diaryl sulfides in which the two aryl rings are identically substituted. Interconversions among the six conformers of the sulfides by ring-flip mechanisms are depicted in Scheme I. The disrotatory "ring-flipping" or "gear-meshing" interconversions, represented by pathways A, B, C, D and A′, B′, C′, D′ (Scheme I) have low activation barriers. The room-temperature NMR spectra of sulfides **3**-**6**, in which two peaks for nonequivalent methyl groups are seen, are explained by reference to these rapid interconversions. In the case of sulfide **3**, broadening of the two methyl peaks was observed by low-temperature NMR. The upper field singlet, which broadens faster than the lower field singlet, splits into two very broad peaks below −82 °C. Increasing separation of the peaks was observed until the temperature reached −110 °C, the lowest permitted by the solubility characteristics of **3** in the solvent system (5:1 (v/v) $CFCl_3$–$CDCl_3$). From the estimated coalescence temperature (−82 °C) for the broad peaks, the upper limit of $\Delta G^{\ddagger}$ of the "gear-meshing" low-barrier processes for sulfide **3** was calculated[7] to be 10.2 kcal mol^{-1} at −82 °C, estimating the chemical shift separation of the two resolved broad absorptions seen at −110 °C to be 3.4 Hz (at 90 MHz).

At temperatures much above room temperature the peaks for the two diastereotopic methyl peaks in each geminal pair coalesce. The exchange processes responsible for this coalescence are the higher barrier interconversions, represented by pathways E, F, and G (Scheme I), the conrotatory "ring-flipping" or "gear-clashing" interconversions. The "gear-clashing" correlation of rotation of the

Scheme I. Mechanism for All the Possible Interconversions for the Ar_2S System[a]

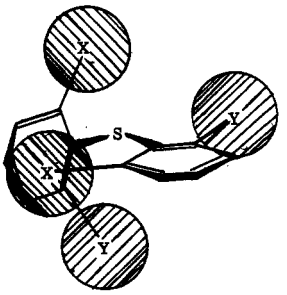


[a] Substituents X and Y are the bulky ortho substituents of compounds **3**-**6**. Two pairs of the conformers are identical, as indicated.

(6) (a) Pirkle, W. H.; Muntz, R. L.; Paul, I. C. *J. Am. Chem. Soc.* **1971**, *93*, 2817. (b) Pirkle, W. H.; Sikkenga, D. L. *J. Org. Chem.* **1975**, *40*, 3430.
(7) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.
(8) Higher temperatures could not be reached because of the thermal instability of the samples.
(9) (a) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

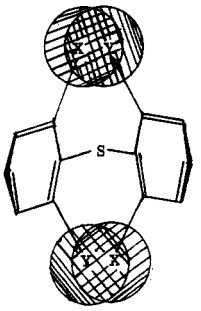
two aryl rings provide the largest steric interaction in the transition state, that between the two ortho substituents which must slip past each other in the transition state for this mode of correlated internal rotation.

The transition states (e.g., B*) for the lowest energy disrotatory processes (e.g., pathway B of Scheme I) have one aryl ring perpendicular to the C–S–C plane and one essentially in the plane.



B*

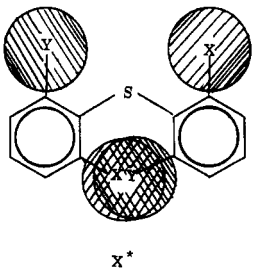
The most important steric interactions, those between the ortho substituent of the coplanar ring and carbons of the perpendicular ring, is relieved by an opening of the C–S–C angle. The bending of the long C–S bonds is relatively easy. No such mechanism for the relief of strain is available for the higher energy transition state E* (e.g.,



E*

the transition state for pathway E of Scheme I). Since all four of the ortho positions are occupied by bulky substituents, it is not possible to relieve the steric interactions in E* by bending the C–S bonds. An examination of molecular models makes it clear that the required deformation of bonds joining ortho substituents X or Y to the ring, or bond deformations within the bulky ortho substituents, since these deformations are much nearer the site of the interaction and since they involve bonds less easily bent than the C–S bonds, are energetically much more costly than in B*.

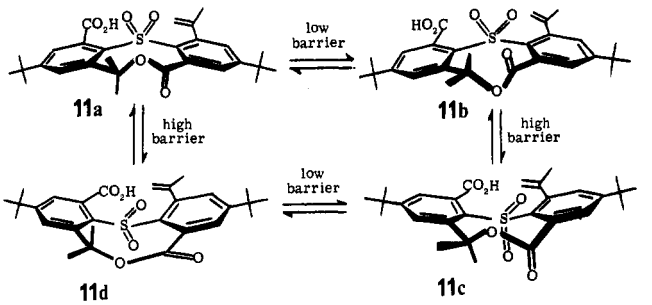
A referee has suggested that a third sort of process might be considered for ring conrotation via a transition state with both rings in the C–S–C plane (e.g., X*).



X*

Transition state X*, for the one-step interconversion of structures at the upper right and lower left of Scheme I, can be seen from an inspection of molecular models to be prohibitively high in energy. The bulky substituents are

Scheme II

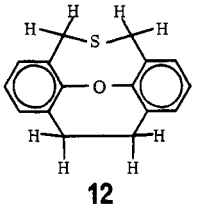


essentially superposed in the transition state unless very large distortions of bond angles are introduced into the molecule.

We therefore suggest that the low-energy process frozen out at low temperature in these compounds occurs via transition states for disrotation such as B*. The higher energy process for which evidence is seen at high temperature is the conrotation via transition states such as E*. Since these two processes completely scramble the methyl groups, it is not possible to gain evidence for the still slower processes which might occur via transition states of type X*.

Isomerism and isomerization in the Ar_2SO_2 system may be analyzed in the same manner as that employed for the Ar_2S system. Thus the mechanisms for the interconversions among the six conformers of the sulfone are analogous to those described for the sulfide case (Scheme I). In the case of sulfones **7–10**, the room-temperature NMR observation, in which two methyl peaks are seen, reflects rapid "gear-meshing" interconversions, A, B, C, D and A′, B′, C′, D′. The coalescence of the two nonequivalent methyl peaks in these sulfones, however, corresponds to a higher activation barrier than that determined for the corresponding sulfides (Table I). The addition of two oxygen ligands to the sulfur in the sulfone apparently gives rise to a greater degree of steric interference to the rotations of the two aryl rings, the "gear-clashing" interconversions E–G. Hydrogen bonding between the sulfonyl oxygens and the hydroxy groups or attractive interactions between oxygen and sulfur may also be important in stabilizing ground-state conformations relative to the transition states for "gear-clashing" synchronous relations of the two rings.

Conformational Interconversion Processes in a Cyclic Diaryl Sulfone 11. The coalescence of the two nonequivalent geminal methyls of the eight-membered-ring lactone sulfone **11** involves conformational interconversions in the eight-membered ring. An analogous NMR study of a quadruply ortho-substituted diphenyl ether, **12**, has



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been reported.[10] Both the methylene AB quartet and the AA′BB′ multiplet for the ethylene bridge of **12**, which are seen at room temperature, coalesce at 130 °C, with a $\Delta G^{\ddagger}$ of 20.0 kcal mol^{-1}. This observation was explained by invoking processes involving oxygen inversion and ring inversion. The mechanism that we propose, in the case

(10) Gordon, A. J.; Gallagher, J. P. *Tetrahedron Lett.* **1970**, 2541.

of lactone sulfone **11**, involves only eight-membered-ring inversion; inversion of sulfonyl sulfur is an unlikely and unnecessary component of this process (Scheme II).

The room-temperature ^1H NMR of **11** shows absorptions postulated to be averages for two conformations whose interconversion occurs via low activation energy processes involving primarily changes in conformation of the three-atom bridge (**11a** ⇄ **11b** or **11c** ⇄ **11d**). Conformers **11a** and **11c** (and also **11b** and **11d**) are enantiomeric. Since **11a** and **11b** are interconverted at ambient temperatures, the two enantiomeric equilibrating systems give rise to only two methyl peaks in the NMR spectrum. At the coalescence temperature the NMR observation is explained by postulating a process of ring inversion of the eight-membered ring, involving a rotation about the sulfur-aryl bond (**11a** ⇄ **11d** and **11b** ⇄ **11c**). The latter process, a ring inversion involving the one-atom (sulfur) bridge, which interconverts the two enantiomeric systems, occurs with a higher activation energy (19.4 kcal mol^{-1}).

Conclusion

We have shown here that diaryl sulfides, having each benzene ring doubly ortho substituted, show the effects of a high level of steric interference. Isomerization of the possible conformers resulting from restricted internal motions, via the "gear-clashing" pathways, requires a high activation energy. The conformational interconversions are further slowed for the corresponding sulfones, an effect which may reflect the additional transition-state steric effects of the two sulfonyl oxygen atoms.

Explanations for our observations on sulfones may be complicated by the possibility in some conformations of attractive interactions between the nucleophilic oxygen atoms of the ortho-substituents and the electrophilic sulfonyl sulfur. Evidence for such interactions will be discussed in a later paper, including chemical evidence and evidence adduced from an X-ray structure determination for sulfone **7**.

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Registry No. **3**, 62558-12-7; **4**, 62558-13-8; **5**, 75893-97-9; **6**, 78480-10-1; **7**, 78479-63-7; **8**, 78480-11-2; **9**, 78479-64-8; **10**, 78480-12-3; **11**, 75893-86-6.

Ketalization of Dihydroxy Sulfones (8-S-4 Species) by Cyclodehydration To Form Spirobicyclic Oxysulfurane Oxides (10-S-5 Species)[1]

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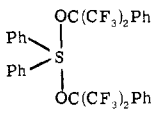
Dihydroxy sulfones **6** and **7** react with the dehydrating agent $Ph_2S(OC(CF_3)_2Ph)_2$ (**1**) to give sulfurane oxides **8** and **9**, respectively. These reactions are thought to be the first examples of the direct ketalization of sulfones by dehydration. A possible mechanism for this ketalization is proposed, and related evidence is discussed. The crystal and molecular structures of **6** are solved by X-ray crystallographic techniques (R = 0.079), and reveal a distorted tetrahedral geometry about sulfur, large steric interactions between the ortho substituents, and short interatomic distances consistent with an attractive electronic interaction between the electrophilic sulfonyl sulfur and the nucleophilic hydroxylic oxygens of **6**.

The number of reported oxysulfuranes has grown rapidly[2] since the preparation of the first isolable acyclic dialkoxysulfurane **1**[2i] and spirosulfurane **2**[2j] were published



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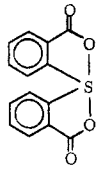


2

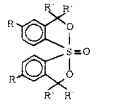
in 1971. The synthesis of **1** involves the oxidative addition of two apical oxygen ligands to a sulfur(II) atom, a process which can be represented in eq 1. The cyclodehydration

$$R_2S + 2\ ^-OR' \xrightarrow{[O]} R_2S(OR')_2 \qquad (1)$$

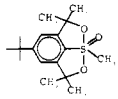
of a dihydroxy sulfoxide to give a dioxysulfurane is a special case of eq 2. The two routes shown in eq 1 and 2 are usually used to prepare other oxysulfuranes.

$$R_2S{=}O + 2HOR' \xrightarrow{-H_2O} R_2S(OR')_2 \qquad (2)$$

In contrast to oxysulfuranes, only a few oxysulfurane oxides such as **3**,[3] **4**,[4] and **5**[5] have been reported. These



3 R = C(CH3)3; R' = CF3
4 R = H; R' = CH3



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sulfurane oxides were synthesized by direct oxidation of their parent sulfuranes. Pathways such as those shown

(1) The designations of 10-S-5 and 8-S-4 are part of the N-X-L nomenclature system. See: Perkins, C.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

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(5) Lau, P. H. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5490.

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