Acknowledgment. We gratefully acknowledge helpful discussions with Professor Sidney W. Benson concerning thermochemical estimates for radicals and neophyl-like rearrangement intermediates and with Dr. Donald M. Schoengold for gas chromatographic–mass spectral analysis and assistance in setup and operation of a capillary GC system.

Registry No. 1, 75421-36-2; 2, 75421-37-3; 3, 75421-38-4; 4, 69339-77-1; 5, 75421-39-5; 6, 75421-40-8; 8, 75494-99-4; 9, 31987-29-8; 10, 75495-00-0; 11, 75421-41-9; 12, 75421-42-0; *tert*-butyl 1-methylindan-2-percarboxylate, 75421-43-1; *tert*-butyl 2-methylindan-1-percarboxylate, 75421-44-2; *tert*-butyl 1-indanperacetate, 75421-45-3; *tert*-butyl tetralin-2-percarboxylate, 75421-46-4; *tert*-butyl 2-indanperacetate, 75421-47-5; *tert*-butyl tetralin-1-percarboxylate, 75421-48-6; indene, 95-13-6; 1-methylindan, 767-58-8; 3-methylindene, 767-60-2; *cis*-1,2-dimethylindan, 39172-70-8; *trans*-1,2-dimethylindan, 70282-84-7; 1-methylindene, 767-59-9; methyl 1-methylindan-2-carboxylate, 75421-49-7; 1-methyl-2-*tert*-butoxyindan, 75421-50-0; 2-methylindan, 824-63-5; 2-methylindene, 2177-47-1; 2,2'-dimethyl-1,1'-biindan, 75421-51-1; *trans*-1-*tert*-butoxy-2-methylindan, 75421-52-2; methyl 2-methylindan-1-carboxylate, 75421-53-3; *cis*-1,3-dimethylindan, 26561-33-1; *trans*-1,3-dimethylindan, 40324-83-2; 1-methyleneindan, 1194-56-5; 2-methyleneindan, 68846-65-1; 1-ethylindan, 4830-99-3; tetralin, 119-64-2; 1,2-dihydronaphthalene, 447-53-0; 1,4-dihydronaphthalene, 612-17-9; 2-methyltetralin, 3877-19-8; 1-methyltetralin, 1559-81-5; naphthalene, 91-20-3; *meso*-1,1'-bitetralyl, 75421-54-4; *dl*-1,1'-bitetralyl, 75421-55-5; 2-ethylindan, 56147-63-8; 1-*tert*-butoxytetralin, 75421-56-6; methyl tetralin-1-carboxylate, 17502-86-2; *cis*-1-*tert*-butoxy-2-methylindan, 75421-57-7.

Conformation in Solution of Sterically Hindered Sulfoxide and Sulfone Alcohols

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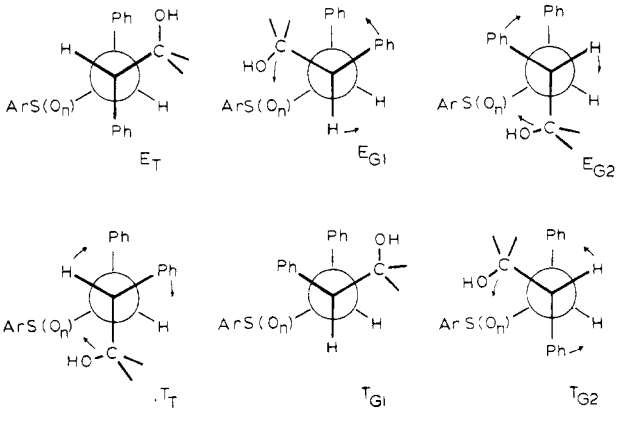
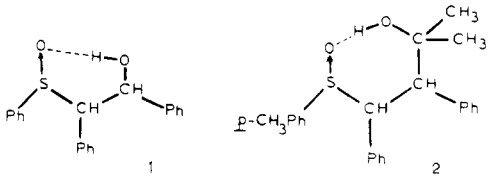
The conformations of the isomeric 2-methyl-3,4-diphenyl-4-(4-methylthiophenoxy)-2-butanols, 2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanols, and 2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanols have been studied by means of NMR and infrared spectroscopy. In contrast to the 2-(benzenesulfinyl)-1,2-diphenyl-1-ethanols of a previous study, three of the four isomeric alcohols showed evidence for intramolecular hydrogen bonding in solution, although a seven-membered ring results upon hydrogen bonding. However, in one isomer, the hydrogen bonding is weak. In another isomer, a strong hydrogen bond is present, although hydrogen-bond formation occurs at the expense of considerable deformation of the molecule from the usual type of structure having dihedral angles close to 60°. X-ray crystallographic data also show a tendency of this type of molecule to adopt a solid-state conformation having markedly variable dihedral angles.

Molecules having possibilities for intramolecular hydrogen bonding offer some of the most interesting problems in acyclic conformational analysis.[1] The question of interest concerns the extent to which intramolecular hydrogen bonding is able to overcome the repulsive interactions of large groups and force the population of otherwise disfavored conformers.

In these studies, the sulfoxide group is useful as a hydrogen-bond acceptor. Sulfoxides are among the strongest acceptors; in fact, addition of dimethyl sulfoxide to water results in the liberation of considerable heat.[2b] The sulfoxide also is chiral, and the effect of configuration at sulfur is of interest. In previous studies of sulfoxide alcohols (i.e., **1**),[3] internal hydrogen bonding prevailed in only

Scheme I





(1) (a) G. Dana, M. Chuche, and M-R. Monot, *Bull. Soc. Chim. Fr.*, 3308 (1967); (b) J. Basselier, J.-J. Canceill, and J. Jacques, *ibid.*, 1906 (1963); 1024 (1967); (c) S. L. Spassov, *Tetrahedron*, **25**, 3631 (1969), and related papers; (d) R. A. Auerbach and C. A. Kingsbury, *ibid.*, **27**, 2069 (1971); (e) M. Stiles, R. R. Winkler, Y. Chang, and L. Traynor, *J. Am. Chem. Soc.*, **86**, 3337 (1964); (f) L. P. Kuhn, *ibid.*, **74**, 2492 (1952), and related papers; (g) K. D. Carlson, D. Weisleder, and M. E. Daxenbichler, *ibid.*, **92**, 6232 (1970); (h) C. A. Kingsbury, *J. Org. Chem.*, **35**, 1319 (1970); (i) W. E. Truce, and T. C. Klinger, *ibid.*, **35**, 1834 (1970); (j) A. L. Ternay, Jr., and D. M. Chasar, *ibid.*, **33**, 2237 (1968), and related papers; (k) D. W. Chasar, *ibid.*, **41**, 3111 (1976); (l) M. E. Munk, M. K. Meilahn, and P. Franklin, *ibid.*, **33**, 3480 (1968); (m) M. K. Meilahn, C. N. Statham, J. L. McManaman, and M. E. Munk, *ibid.*, **40**, 3551 (1975); (n) J. Sicher, M. Cherest, Y. Gault, and H. Felkin, *Collect. Czech. Chem. Commun.*, **28**, 72 (1963).

(2) (a) D. Martin, A. Weise, and H.-J. Niclas, *Angew. Chem., Int. Ed. Engl.*, **6**, 318 (1967); (b) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964); (c) I. M. Kolthoff and M. K. Chantooni, *J. Am. Chem. Soc.*, **98**, 5063 (1976); (d) H. H. Szmant, in "Dimethylsulfoxide", S. Jacob, E. Rosenbaum, and D. Wood, Eds., Marcel Dekker, New York, 1971, p 3, 21, 33; (e) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(3) C. A. Kingsbury and R. A. Auerbach, *J. Org. Chem.*, **36**, 1737 (1971).

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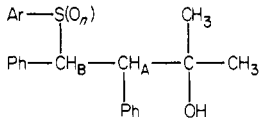
Table I. ^{1}H NMR Chemical Shifts and Coupling Constants of 3-10



compd	solvent	J_{AB}, Hz	chemical shift, ppm CH_3	CH_3	H_A	H_B	OH
3, threo sulfide	1.0% $CDCl_3$[e]	10.8	1.07	1.55	3.41	4.55	3.9[a]
	2.5% benzene	10.4	1.23	1.49	3.47	4.65	
	2.5% Me_2SO	7.8					
4, erythro sulfide	2.0% $CDCl_3$[f]	7.5	1.12	1.25	3.19	4.78	2.13[a]
	2.5% benzene	6.5	1.14	1.23	3.11	4.92	2.37
	2.5% Me_2SO-d_6	7.5					
5, erythro sulfoxide, mp 185 °C	1.0% $CDCl_3$	12.3	0.87	1.08	3.74	4.03	1.28
	benzene	insoluble					
	2.5% Me_2SO-d_6	11.9[d]					
	2.5% TFA-$CDCl_3$[c]	12.3	1.00	1.19	3.86	4.16	
6, erythro sulfoxide, mp 151 °C	1.0% $CDCl_3$	2.8	1.04	1.60	3.19	4.71	5.25[b]
	2.0% benzene	2.3	1.16	1.69	3.09	4.75	
	0.4% Me_2SO	7.1					
	2.5% TFA-$CDCl_3$[c]	4.9	1.16	1.55	3.32	4.98	
7, threo sulfoxide, mp 137 °C	1.0% $CDCl_3$	10.6	1.27	1.48	3.83	4.37	ca. 2.1[a]
	2.0% benzene	10.8	1.35	1.55	4.15	4.34	
	2.5% Me_2SO	10.8					
8, threo sulfoxide, mp 159 °C	1.0% $CDCl_3$[g]	6.9	1.22	1.31	3.96	4.65	4.88[b]
	2.5% benzene	6.8	1.38	1.40	4.13	4.89	
	2.5% Me_2SO-d_6	6.4					
	2.5% TFA-$CDCl_3$[c]	6.3	1.29	1.43	4.07	4.90	
9, erythro sulfone	1.0% $CDCl_3$	9.1	1.04	1.04	3.67	4.87	1.55
	benzene	insoluble					
	2.0% Me_2SO-d_6	10.5					
10, threo sulfone	2.5% $CDCl_3$[h]	4.7	1.26	1.26	4.07	4.91	2.9[a]
	benzene	insoluble					
	1.5% Me_2SO-d_6	2.0					
	2.5% TFA-$CDCl_3$[c]	6.1	1.26	1.47	4.22	4.97	

[a] Somewhat concentration sensitive. [b] Concentration insensitive. [c] A stock solution of 0.2 mL of TFA in 3.9 mL of $CDCl_3$ was used. More concentrated TFA solutions tended to produce broadening. [d] Tentative value; an accurate determination is impossible. [e] J_{AB} = 12.0 Hz at -68 °C. For the trimethylsilyl derivative J_{AB} = 5.7 Hz (ambient temperature). [f] J_{AB} = 8.1 Hz at -60 °C. [g] The chemical shifts of H_A and H_B are δ 3.7 and 4.3, respectively, for the trimethylsilyl derivative (J_{AB} = 2.1 Hz). [h] The chemical shifts of H_A and H_B are δ 3.87 and 4.82, respectively, for the trimethylsilyl derivative (J_{AB} = 1.6 Hz).

one of the four diastereomers. Although the internal hydrogen-bonded structure forms a six-membered ring, a rather unfavorable geometry is evidently one reason for the lack of hydrogen bonding in more than one isomer. The hydroxyl is not able to approach the end of the S–O bond due to the rather long C–S bond (ca. 1.84 Å) and possibly a rather large C–S–O bond angle (107 to 112°).[2,5,6] In the sulfoxide alcohols of the present study (2), the longer hydrocarbon chain has the effect of eliminating these geometric constraints. However, formation of a seven-membered ring is required to close the hydrogen bond, and entropy restrictions are increasingly unfavorable compared to system 1.[7] At the outset of the study, it was believed that the *gem*-dimethyl group in 2 would facilitate hydrogen bonding through restriction of conformational possibilities for the hydroxyl group.[8]

In this study, the conformation of the isomeric sulfoxides 5–8 will be compared to that of the corresponding sulfides 3, 4 and sulfones 9, 10. The sulfide and sulfone groups are weaker hydrogen-bond acceptors,[1i,3,9] although the sulfides can hydrogen bond through a six-membered ring, which enhances the probability of hydrogen bonding.

The conformations of the molecules of interest are shown in Scheme I in Newman projections. The predominant conformation is qualitatively identified through ^{1}H NMR coupling constants. Coupling constants of 10–13 Hz are taken as indicative of a strong preference for a conformer with trans vicinal hydrogens, and values in the 1–3-Hz range indicate gauche hydrogens.[10] The NMR data are listed in Table I. Carbon-13 NMR data were also collected but were not particularly informative.[11]

In many sets of diastereomers, stronger hydrogen bonding is found for the threo isomer. Partial internal

(4) The literature is rich in examples of stable internal hydrogen bonding occurring through six-membered rings; cf. M. Tichy, *Adv. Org. Chem.*, 5, 115 (1965).

(5) B. B. Jarvis, S. D. Dutkey, and H. L. Ammon, *J. Am. Chem. Soc.*, 94, 2136 (1972); see also, E. Block, E. R. Corey, R. E. Penn, T. L. Renken, and P. F. Sherwin, *ibid.*, 98, 5715 (1976).

(6) By extrapolation of the findings of L. Joris and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 90, 4599 (1968), the geometry shown should be quite unfavorable.

(7) L. P. Kuhn, P. v. R. Schleyer, W. F. Baitinger, and L. Eberson, *J. Am. Chem. Soc.*, 86, 650 (1964), show that hydrogen bonding through a large ring is relatively improbable, though energetically favorable.

(8) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, 25, 701 (1960).

(9) P. von R. Schleyer and R. West, *J. Am. Chem. Soc.*, 81, 3164 (1959); H. H. Szmant and J. J. Rigau, *J. Org. Chem.*, 31, 2288 (1966).

(10) A. A. Bothner-By, *Adv. Magn. Reson.*, 1, 115 (1965); see also T. P. Forrest, *J. Am. Chem. Soc.*, 97, 2628 (1975); E. W. Garbisch and M. Griffith, *ibid.*, 80, 6543 (1968).

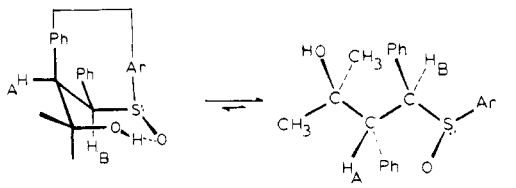
(11) For the sulfides 3 and 4, C_3 occurred at 60.9 and 58.7 ppm and C_4 at 57.1 and 56.9 ppm, respectively. For the sulfoxides 5, 6, and 8, C_3 is 71 to 73 ppm and C_4 is 73.8–75.0 ppm. For the sulfones, C_3 is 55.4 and 58.7 ppm and C_4 is 75.5 and 71.2 ppm (probable assignments, but not certain in the latter case). For other studies of the ^{13}C NMR spectra of sulfides, etc., see M. S. Chauhan and I. W. J. Still, *Can. J. Chem.*, 53, 2880 (1975); G. Barbarella, P. Dembach, A. Garbesi, and A. Fava, *Org. Magn. Reson.*, 8, 108 (1976).

rotation about bonds analogous to C_3–C_4 in **2** occurs, permitting closer approach of hydroxyl to the hydrogen-bond acceptor.[12] This internal rotation also relieves repulsions between large groups, e.g., between Ph groups in conformer T_T (Scheme I) or between Ph and $ArSO_n$ in conformer T_{G2}. However, for the erythro isomers, internal rotation favoring hydrogen bonding *increases* the repulsive interactions of large groups, as between Ph and Ph in E_{G1} or E_{G2}.[1]

In agreement with these expectations, the hydroxyl infrared absorptions for the threo sulfide **3** occur at 3572 (w) and ca. 3450 (br, s) cm^{-1}. For *erythro*-**4** absorptions occur at 3587 (m) and 3490 (m) cm^{-1}. These concentration-insensitive absorptions indicate a larger frequency shift ($\Delta\nu$) relative to the usual position for a free tertiary hydroxyl (ca. 3610 cm^{-1})[4] for the threo isomer, indicative of stronger hydrogen bonding for this isomer.[1] The IR peaks at ca. 3450 cm^{-1} are most likely due to S··HO association; other peaks are probably due to association with solvent, or an OH··π interaction.[4,13]

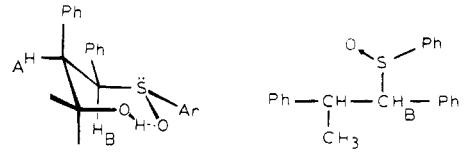
The NMR data are in agreement with the IR data. Thus, *threo*-**3** shows a large J_{AB} (ca. 10 Hz) in $CDCl_3$ or benzene, indicative of a strong preference for T_T in which internal hydrogen bonding is highly probable. The chemical shift of the OH in **3** is highly deshielded (δ 3.9) compared to that of *erythro*-**4** (δ 2.1), as expected for stronger hydrogen bonding in the former case.[14] *erythro*-**4** shows a NMR J_{AB} of 7.5 Hz indicative of a mixture of conformers, including a substantial population of E_T in which internal hydrogen bonding is impossible due to trans donor and acceptor groups. For **4**, the IR spectrum shows a sizable peak (3587 cm^{-1}) due to a "free" hydroxyl (i.e., an OH not hydrogen bonded to S), as expected for conformer E_T. For *threo*-**3**, a change of solvent to Me_2SO results in a large change in J_{AB}. Powerful hydrogen-bonding solvents such as Me_2SO disrupt some types of internal hydrogen bonds, giving rise to abrupt changes in conformational weights.[3] For **4**, however, Me_2SO has little effect on J_{AB}. The weak internal hydrogen bond may not significantly affect the choice of conformation.[1h]

The high-melting erythro sulfoxide[15] **5** shows no tendency for internal association. The J_{AB} (12 Hz) indicates a strong preference for **5b** in which the SO and OH groups are distant. The zigzag type of conformation, such as **5b**, is quite widespread in acyclic diastereomers.[16] The chemical shift of the OH is shielded (δ 1.28), in agreement with its presumed location over the face of one phenyl ring.[17] The infrared spectrum shows broad OH absorptions at ca. 3590 and 3575 cm^{-1}, which are quite different from hydrogen-bonded (to S–O) hydroxyl absorptions (ca. 3300–3400 cm^{-1}) observed in other molecules. One reason for the lack of intramolecular hydrogen bonding is seen in an alternative conformer **5a** which suffers from an unfavorable 1,3-interaction.[18]



5a **5b** (E_T)

In contrast to **5**, the low-melting erythro sulfoxide **6** is



6a (E_{G2}) **11**

quite strongly internally hydrogen bonded. The J_{AB} value for **6** (2.8 Hz) indicates a strong preference for a conformer having gauche hydrogens. The OH resonance (δ 5) is strongly deshielded, as expected for a firmly hydrogen-bonded hydroxyl. A strong, concentration insensitive IR absorption at ca. 3300 cm^{-1} is observed for the hydroxyl. The chemical shifts of H_A and H_B (δ 3.2 and 4.7, respectively) show an inversion of shielding effects compared to H_A and H_B for **5** (δ 3.7 and 4.0).

The decision concerning configuration and conformation at chiral sulfur rests on the chemical shift data for H_A and H_B.[19] For hydrogens β to S–O, the literature is in general agreement that such hydrogens will be deshielded if they lie near in space to S–O, i.e., H_A of **5**. The similarity of S–O in anisotropy characteristics to an acetylene has been mentioned[20] but also criticized.[19,21-23]

For hydrogens α to S–O, no general agreement exists in the literature. Recently, Sataty has shown that hydrogens cis to S–O in certain benzothiolane oxides are more often shielded than deshielded (conformation of S–O was not determined, however).[19] Johnson,[21] Fraser,[22] and Webber[23] emphasize the effect of the lone pair of sulfur, rather than that of oxygen, i.e., hydrogens lying anti to the lone pair are expected to be shielded.[24] However, in the compounds of the present study, α hydrogens that lie near S–O appear to be *de*shielded, despite the lone-pair effect (e.g., in **6**, H_B, δ 4.71). In the present study, such deshielded hydrogens occur in internally hydrogen-bonded compounds. It is quite possible that the anisotropy of the O–H··O structure plays a role. The findings of Grosescu et al. in maleic acid do indicate such a deshielding effect.[25] A model compound (**11**) was tested with external hydrogen-bond donors. In this conformationally mixed molecule, H_B lies near SO at least part of the time and thus would experience the

(12) (a) L. Eberson, in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, London, 1969, p 211; (b) L. L. McCoy, *J. Org. Chem.*, **30**, 3762 (1965), and related papers.

(13) (a) M. Oki, H. Iwamura, J. Aihara, and H. Ida, *Bull. Chem. Soc. Jpn.*, **41**, 176 (1968); (b) H. Iwamura, *Tetrahedron Lett.*, 2227 (1970).

(14) (a) J. C. Davis, Jr., and K. K. Deb, *Adv. Magn. Reson.*, **4**, 201 (1970); (b) O. P. Yablonskii, *Zh. Fiz. Khim.*, **49**, 2538 (1975).

(15) The terms "erythro" and "threo" refer to configuration at carbon, not sulfur.

(16) For an exception, see C. A. Kingsbury, R. P. Hutton, and D. L. Durham, *J. Org. Chem.*, **43**, 4450 (1978).

(17) D. C. Kleinfelter, *J. Am. Chem. Soc.*, **89**, 1734 (1967), indicates that an OH··π hydrogen bond may give rise to a shielded resonance for OH due to the aromatic ring current. For other commentary, see R. J. Ouellette, D. L. Marks, and D. Miller, *ibid.*, **89**, 913 (1967).

(18) (a) P. E. McMahon and W. C. Tincher, *J. Mol. Spectrosc.*, **15**, 180 (1965); (b) A. B. Dempster, K. Price, and N. Sheppard, *Chem. Commun.*, 1457 (1968).

(19) I. Sataty, *Org. Magn. Reson.*, **6**, 8 (1974).

(20) R. A. Archer, and P. V. DeMarco, *J. Am. Chem. Soc.*, **91**, 4530 (1969); R. D. G. Cooper, P. V. DeMarco, J. C. Cheng, and N. D. Jones, *ibid.*, **91**, 1408 (1969).

(21) W. O. Siegl and C. R. Johnson, *Tetrahedron*, **27**, 341 (1971).

(22) R. R. Fraser and F. J. Schuber, *Can. J. Chem.*, **48**, 633 (1970).

(23) A. B. Foster, T. D. Inch, M. H. Quader, and J. M. Webber, *Chem. Commun.*, 1086 (1968). See also R. M. Dodson, *J. Org. Chem.*, **35**, 3520 (1970).

(24) However, some of the criticism of the acetylenic type of anisotropy of the SO group was made without knowledge of the resently established varying type of anisotropy of the C–S and C–$S(O_2)$ bonds vis-à-vis C–S(O); cf. S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Am. Chem. Soc.*, **97**, 1468 (1975).

(25) R. Grosescu, A. M. Achlama, U. Haberlen, and H. W. Spiess, *Chem. Phys.*, **5**, 119 (1974).

anisotropy of the hydrogen bond, when formed. Addition of a threefold excess of phenol to **11** did indeed give rise to a $\Delta\delta = 0.17$ ppm deshielding of H_B. The effect probably would be larger in a rigid, internally hydrogen-bonded structure.

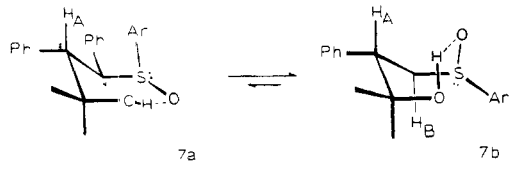
The X-ray crystallographic structure (vide infra) of one of these sulfoxides disclosed bond angles at sulfur that were suggestive of a high degree of s character in the lone-pair orbital. Thus, the lone pair at sulfur may not be highly anisotropic in this particular group of aryl sulfoxides. Previous studies in which the shielding effect of the lone pair was postulated were done with alkyl sulfoxides.[20-22] In **5**–**8**, the S–Ar group, of course, affects the chemical shifts of H_A and H_B due to its own anisotropy. This aromatic group usually is oriented edgewise with respect to the C-H_B bonds in various compounds and is thus deshielding. Whatever the orgin, the S–O group appears to deshield H_B in **5**–**8** in cases where S–O is near in space to H_B. Similar findings occur in molecules such as **11**.

An unusual feature of the NMR spectrum of **6** is an upfield peak (δ 6.4) due to a single aromatic hydrogen. This resonance moves downfield in TFA solutions. Models suggest that one ortho hydrogen of the pseudoaxial C_3 Ph group lies near sulfur. The shielding of this hydrogen may be an expression of the lone-pair effect.

The conformation of **6**, thus, appears to be as indicated, i.e., gauche hydrogens H_A and H_B, of which H_A is distant from S–O, in the strongly hydrogen-bonded S–O··HO structure. **6** undergoes a large increase in J_{AB} upon changing from $CDCl_3$ to Me_2SO as solvent (Table I), indicative of a greater population of conformer E_T. A smaller increase in J_{AB} is noted in $CDCl_3$–TFA solutions. TFA either protonates or hydrogen bonds to S–O,[2a] thus reducing its ability to accept an internal hydrogen bond.

The low-melting threo sulfoxide **7** is characterized by a very high J_{AB} (10.6 Hz), indicative of a high population of T_T in which internal hydrogen bonding should be present. However, the chemical shift of the OH (δ 2.1) is not suggestive of strong hydrogen bonding. The IR spectrum shows peaks at 3585 (w) and 3420 (s) cm^{-1}.[25] The shift in hydroxyl absorption due to hydrogen bonding ($\Delta\nu$ ca. 190 cm^{-1}) is indeed less than that found for **6** and **8** ($\Delta\nu$ ca. 290 cm^{-1}) but does indicate S–O··HO association.

In the possible conformers **7a** or **7b**, hydrogen bonding

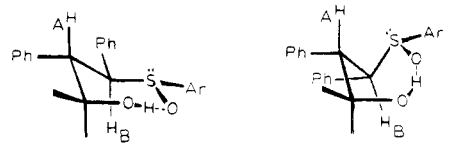


7a 7b

should be weaker in **7b** due to poor geometry. In **7a**, Ar lies gauche to C_4Ph and to C_3. The small Ar–S–C_4 bond angle (ca. 99°) causes Ar to impinge upon these gauche groups quite severely. If **7a** were dominant, H_A would be shielded as it lies over the face of S–Ar. In fact, H_A is deshielded, probably by S–O. On the other hand, H_B is *not* deshielded (as expected in conformer **7a**, if S–O is indeed deshielding). In toto, the evidence favors a substantial population of **7b**.

The high-melting threo sulfoxide **8** represents a rather unusual case. The J_{AB} of 6.9 Hz could result from nearly equal populations of two conformers having trans and gauche hydrogens, respectively. Alternatively, this J_{AB} value could be due to a high population of one conformer having highly atypical dihedral angles. The IR spectrum of **8** shows that this molecule is strongly hydrogen bonded (ν_{OH} ca. 3340 cm^{-1} plus a very weak "free" hydroxyl absorption).[26] In agreement, the NMR resonance of OH (δ 4.9) is deshielded and not significantly concentration dependent. Addition of a threefold excess of phenol leads to a spectrum showing separate OH resonances for phenol and **8**, despite a rather small chemical-shift separation. The lack of effect of Me_2SO and TFA on J_{AB} also suggests that the hydrogen bond is not easily broken. The J_{AB} value for the (non hydrogen bonded) trimethylsilyl derivative is 2 Hz.

Hydrogens A and B *both* occur at relatively low field (δ 3.96 and 4.65, respectively), which suggests that both hydrogens experience the anisotropy of the SO group, on the average, although other deshielding mechanisms are also possible. The pseudochair conformation **8a** is seemingly



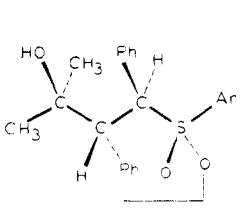
8a (T_T) 8b

stable and serves as the entry point for the discussion of conformation. However, in **8a** H_A is distant from SO and not likely to be deshielded by this group. Molecular models show that **8** suffers from a disadvantage not obvious in the structural drawing **8a**. The two oxygens lie in virtual contact with one another. Insufficient space exists between oxygens to accommodate a hydrogen-bonded hydrogen. Eberson and also McCoy have discussed the consequences of too small O··O separations on hydrogen bonding.[12] In general, separations less than 2.4 Å strongly destabilize hydrogen bonding.

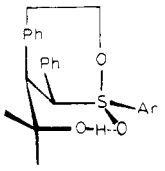
The strong hydrogen bond in **8** could arise in one of three ways: (i) by deformation of the C–C–C backbone of the pseudochair in the basic structure **8a**, thus creating sufficient O··O spread for a hydrogen bond; (ii) by torsional changes which would thus permit a more favorable O–H··O geometry at the expense of introducing unfavorable nonbonded interactions among other groups; or (iii) by a combination of the previous factors. The carbon-13 NMR spectrum did not show any grossly unusual chemical shifts for **8** that could be ascribed to bond angle deformations. On the other hand, X-ray crystallographic data do show that **8** possesses highly unusual dihedral angles in the solid state. Given the propensity of the molecule to accept rather extreme torsional modifications, a skewed conformer such as **8b** seems to fit the data the most closely. Models show that both H_A and H_B in **8b** are sufficiently close to SO to be deshielded. However, it is possible that **8** occupies a group of conformations having rather similar dihedral angles of which **8b** is only one contributor. It is difficult to believe that **8b** represents a deep potential minimum in view of the juxtaposition of various groups.

The erythro sulfone **9** prefers the extended conformation **9a**, as shown by the rather high J_{AB}. Sulfones are known to be rather weak hydrogen-bond acceptors, but, nevertheless, the preference of **9a** over **9b** is surprising, since even a weak internal hydrogen bond should afford some stabilization. Entropy considerations and perhaps the

(26) The changes in SO stretching frequency complement the variations in OH stretch upon formation of internal hydrogen bonds. Barnard et al.[2e] observed a change in SO absorption from 1055 to 1035 cm^{-1} upon hydrogen-bond formation. In the present cases, two peaks were usually observed in the SO region of the spectrum; for **6** and **8**, which are strongly intramolecularly hydrogen bonded, the SO stretch is shifted to lower values: 1021 and 1011 cm^{-1} and 1026 and 1018 cm^{-1}, respectively. For **5** (not hydrogen bonded) a broad absorption at 1042 cm^{-1} is observed, whereas for **7** (weakly hydrogen bonded) peaks at 1039 and 1015 cm^{-1} are found. The higher frequency absorption of each pair is tentatively assigned as the SO stretch for each pair.



9a



9b

necessity for forming a skewed conformer similar to **8b** perhaps outweigh the stabilization gained by hydrogen bonding.

The threo sulfone **10** also exhibits some unusual features. The J_{AB} (5 Hz) again could be due to a predominance of T_{G1} and/or T_{G2}, plus some admixture of T_T, or it could be due to a predominance of a conformer with skewed dihedral angles such as **8b**. The IR spectrum shows peaks at 3585 (m) and at ca. 3500 (s) cm^{-1}. The latter is consistent with SO_2··HO hydrogen bonding.[1i,27] This tends to rule out a high population of T_{G1} in which $ArSO_2$ and HO are trans. However, a high population of T_{G2} also seems unlikely in view of the congested positions of the large groups ($ArSO_2$ and $[(CH_3)_2(HO)C]$). A predominance of conformers similar to **8b** again seems likely. In Me_2SO, the internal hydrogen bond is disrupted, and J_{AB} becomes very low (ca. 2 Hz). The trimethylsilyl derivative shows a similar J_{AB}, indicative of a dominance of T_{G1}.

In order to obtain precise information on the conformational states of **8** and **10**, X-ray crystallographic analyses were performed. Unfortunately, both **8** and **10** adopted *inter*molecularly hydrogen-bonded structures in the crystal (conformer T_{G1}) that are not directly comparable to the solution conformation. However, dihedral angles are highly skewed in the zigzag solid-phase structure.

In conclusion, the molecules of this study, like previous cases,[1h] display a wide variety of responses to the interplay of two factors: nonbonded repulsions and the stabilization afforded by the internal hydrogen bond, if present. In one case (**8**), the internal hydrogen bond is clearly dominant and insensitive to solvent change despite unfavorable interactions present between other groups. However, in **7**, which differs only in configuration at sulfur, the internal hydrogen bond is weak due to unfavorable geometry, but the hydrocarbon backbone is relatively strain free. In *erythro*-**5**, which has the same configuration at sulfur as **7**, the rather common zigzag shape of the hydrocarbon backbone is found, and no internal hydrogen bonding occurs. In *erythro*-**6**, which has the same configuration at sulfur as **8**, hydrogen bonding is again strong, dictating rather unfavorable interactions of the hydrocarbon backbone. However, this hydrogen bond can be disrupted by hydrogen-bonding solvents. It is noteworthy that strong internal hydrogen bonding is never found if such bonding also gives rise to a severe interaction between S–Ar and another group. In general, configuration at sulfur appears to be a dominant factor in the formation of internal hydrogen bonding. With regard to the hydrocarbon backbone, compounds of the threo configuration form internal hydrogen bonds more readily than erythro compounds. However, the reasons must be a great deal more subtle than the simple internal rotations suggested by Scheme I. The crystallographic data illustrate the close relationship between bond-angle changes and torsional changes as the molecule seeks the minimum energy conformation. In addition, the effects of "conformational transmission" are evident in both the solution and the solid-phase data.[28] A change in configuration or of steric bulk at sulfur ultimately affects distant sites of the molecule.

Experimental Section

Preparation of the Isomeric 2-Methyl-3,4-diphenyl-4-(4-methylthiophenoxy)-2-butanols (3 and 4). To 3,4-diphenyl-3-buten-2-one (22 g, 0.099 mol) and *p*-thiocresol (12.5 g, 0.099 mol) dissolved in ca. 100 mL of methanol was added 1.0 g of sodium methoxide. The solution was then cooled in ice water. After the solution was allowed to stand overnight, a precipitate appeared which was filtered and triturated with equal volumes of acetic acid and then with ethanol. The alcoholic solutions were combined. Additional crops of the product, *erythro*-3,4-diphenyl-4-(4-methylthiophenoxy)-2-butanone (**11**), appeared upon evaporating the methanol and cooling the solution. This material totalled 17.8 g (52%), mp 180–182 °C, and it was pure enough for most purposes. A portion was recrystallized from methylene chloride–ethanol for analysis; mp 182.2–182.7 °C.

Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40. Found: C, 79.63; H, 6.37.

All alcoholic solutions were recombined and evaporated to a small volume. Small additional crops of **11** were obtained. The remaining oily residue partially crystallized on long standing. The oily solid was filtered as well as possible. The mother liquor was taken up in ether, dried ($MgSO_4$), and evaporated to give some additional oily solid. The solids were combined and recrystallized from methanol to yield 1.3 g (4%) of the threo sulfide ketone **12**, mp 90–91 °C. A second crop, mp 75–80 °C, was also obtained (0.8 g). A portion of this product was repeatedly recrystallized for analysis; mp 94–95 °C.

Anal. Calcd for $C_{23}H_{22}OS{\cdot}0.25H_2O$: C, 78.70; H, 6.35. Found: C, 78.71; H, 6.36.

The threo sulfide **12** (4.4 g, 0.013 mol) was added as a solid to a solution of methylmagnesium iodide, prepared from 0.45 g (0.019 mol) of magnesium and 4.4 g (0.021 mol) of iodomethane in 50 mL of ether. The resulting solution was stirred for ca. 4 h and poured onto an ice–NH_4Cl mixture. A precipitate was formed which was taken up in ether, extracted several times with water–NH_4Cl, and dried ($MgSO_4$). The evaporated solution yielded 4.0 g (87%) of **3**, mp 112–114 °C. The material was repeatedly recrystallized from ether for analysis; mp 122–123 °C.

Anal. Calcd for $C_{24}H_{26}OS$: C, 79.51; H, 7.23. Found: C, 79.57; H, 7.18.

The erythro sulfide ketone **11** (8.0 g, 0.029 mol) was similarly treated with an excess of methylmagnesium iodide and added to ice–NH_4Cl to form an oily solid. It was not possible to recrystallize this material adequately, so it was taken up in ether, dried ($MgSO_4$), and chromatographed on a 60 × 2 cm column of silica gel (Baker). The product **4** was obtained (4.2 g, 40%), mp 80–82 °C, from various fractions of benzene–Skelly B eluants. Other fractions, 3.8 g, were oily solids which appeared to be very impure **4** by NMR. A portion of the above product was recrystallized (with difficulty) for analysis, mp 94.2–94.7 °C.

Anal. Calcd for $C_{24}H_{26}OS$: C, 79.51; H, 7.23. Found: C, 79.24; H, 7.15.

Preparation of *erythro*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanols (5 and 6). To 5.0 g (0.014 mol) of **4** in 20 mL of acetic acid was added 1.5 mL of 30% hydrogen peroxide (dropwise) plus a little water. The solution was allowed to stand overnight, and then it was poured into an excess of water. An oily residue formed which partially solidified upon standing. The mixture was extracted with methylene chloride three times. The combined organic layers were extracted with a dilute aqueous solution of NH_4Cl three times and dried ($MgSO_4$); the solvent was evaporated, whereupon crystals formed. The solid was recrystallized by the triangle scheme using combinations of ether, ethanol, and/or methylene chloride as solvents. After several

(27) The referee has suggested the likelihood of a bifurcated hydrogen bond (where OH bonds to both sulfone oxygens simultaneously). While possible, we can neither confirm nor deny this controversial type of bonding; cf. M. D. Joesten and L. J. Schaad, "The Hydrogen Bond", Marcel Dekker, New York, 1974; and P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 4991 (1971).

(28) N. L. Allinger and G. A. Lane, *J. Am. Chem. Soc.*, **96**, 2937 (1974); D. H. R. Barton, F. McCapra, P. J. May, and F. Thudium, *J. Chem. Soc.*, 1297 (1960).

recrystallization cycles, reasonably pure **5** was obtained, mp 176–177 °C, 0.79 g (15%). The best melting point obtained was 184–185 °C.

Anal. Calcd for $C_{24}H_{26}O_2S$: C, 76.16; H, 6.92. Found: C, 76.36; H, 6.87.

After several more recrystallization cycles, **6** was obtained, mp 145–147 °C, 0.43 g (8%). The best melting point obtained was 149–151 °C.

Anal. Calcd for $C_{24}H_{26}H_2S$: C, 76.16; H, 6.92. Found: C, 76.03; H. 6.88.

The remaining mixture of isomers in the recrystallization scheme could no longer be efficiently separated. All fractions were combined and chromatographed on a 1.9 × 30 cm column packed with Florisil by using 5% ethyl acetate in hexane as eluant. An additonal 0.63 g of **6** was obtained in various fractions; mp 143–145 °C.

Preparation of the *threo*-2-Methyl-3,4-diphenyl-4-(4-tolylsulfinyl)-2-butanols (7 and 8). To a solution of **3** (2.7 g, 7.5 mmol) in 20 mL of acetic acid was added 0.91 mL (8 mmol) of 30% hydrogen peroxide along with a little water. After standing overnight, the mixture was heated briefly to ca. 60 °C on a steam bath, cooled, and poured into an excess of water. A precipitate formed that was filtered off. The liquid was extracted three times with methylene chloride, the precipitate was dissolved in the methylene chloride, the organic phase was extracted three times with water–NH_4Cl and dried ($MgSO_4$), and the solvent was evaporated, whereupon crystals formed. The crystals were recrystallized by the triangle scheme as previously. Only the high-melting isomer **8** could be obtained pure. A mixture of other components was observable by TLC, but separation by crystallization or chromatography was unsuccessful, although chromatography did afford an additional quantity of the high-melting isomer **8**, giving a total of 1.7 g (60%), mp 158.6–159.7 °C.

Anal. Calcd for $C_{24}H_{26}O_2S$: C, 76.16; H, 6.92. Found: C, 76.24; H, 6.91.

Unreacted starting material was also recovered, 0.06 g, but the second sulfoxide could not be isolated in this run or in 5–6 additional runs using a variety of oxidants or H_2O_2 in acetic acid at a variety of temperatures. There was a suggestion that the missing sulfoxide **7** easily went to the sulfone, as sulfone and unreacted starting material were frequently found together. Even when **7** was observed by NMR in the reaction mixture, attempted isolation by chromatograpny gave no product.

The low-melting isomer **7** was finally obtained by placing 2.0 g (5.5 mmol) of **3** in 20 mL of methylene chloride and passing NO_2 into the solution intermittently until the distinctive color of NO_2 remained. The solution was allowed to stand for 24 h. The solvent was allowed to evaporate, 5 mL of additional methylene chloride was added, and this was evaporated with gentle heating. A dark oil remained. A small quantity of ethanol was added, and crystallization was induced by cooling and scratching. The precipitate was filtered and recrystallized twice from CH_2Cl_2–ethanol, mp 135–137 °C, 0.06 g (5%). The remaining oil was difficult to crystallize although an additional 0.21 g was obtained (impure with sulfone **10**). The green oil that remained was chromatographed on silica gel, but each fraction was noncrystalline and appeared very impure by NMR.

Mass spectrum (70 eV), *m/e* (relative intensity) 262 (10), 246 (14), 238 (18), 223 (33), 221 (23), 220 (73), 219 (11), 213 (7), 205 (94), 181 (20), 180 (100), 179 (54), 178 (37), 140 (38), 124 (21), 91 (34), and 77 (16). These data may be compared to similar data from **8**: mass spectrum (70 eV), *m/e* (relative intensity) 262 (10), 246 (14), 238 (18), 223 (33), 222 (23), 220 (73), 219 (11), 213 (7), 205 (94), 181 (42), 180 (100), 179 (51), 178 (40), 165 (30), 140 (85), 124 (28), 123 (33), 91 (74), and 77 (29).

Preparation of the Isomeric 2-Methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanols (9 and 10). A solution of 1.0 g (2.6 mmol) of **4** in 20 mL of chloroform was prepared to which was added 1.4 g (ca. 5.3 mmol) of 85% *m*-chloroperoxybenzoic acid (Aldrich). The solution was allowed to stand overnight, and then it was heated on the steam bath until almost all solvent had evaporated. Additional solvent was added and the evaporation process repeated several times. The solution was then added to a dilute solution of potassium carbonate in water and extracted (with difficulty) several times. Each aqueous extract in turn was extracted with methylene chloride, and these extracts were added to the original organic layer. A total of three extraction cycles was carried out, the organic material was dried ($MgSO_4$), and the solvent was evaporated. Cooling and addition of ether produced a precipitate, 0.4 g (39%) of the erythro product **9**, mp 158–160 °C. This was recrystallized from methylene chloride–ethanol; mp 177.0–178.7 °C.

Anal. Calcd for $C_{24}H_{26}O_3S$: C, 73.06; H, 6.64. Found: C, 73.14; H, 6.76.

The threo isomer **10** was prepared by mixing 0.5 g (1.4 mmol) of **3** with 0.59 g (2.9 mmol) of *m*-chloroperoxybenzoic acid in 25 mL of chloroform. The evaporation procedure described above was again used. The product was worked up similarly to **9**. Very slow crystallization from ethanol (some CH_2Cl_2 present) gave long prisms of **10**, mp 177.8–180.2 °C (0.23 g, 45%).

Anal. Calcd for $C_{24}H_{26}O_3S$: C, 73.06; H, 6.64. Found: C, 73.17; H, 6.60.

Spectra. The ^1H NMR spectra were run on a Varian XL-100 instrument at normal probe temperature (ca. 35 °C). Several spectra were run for each compound. The coupling constants were taken from the average of several expansions of the region in question. Some low-temperature work was also done in an attempt to freeze out different conformers, although this was unsuccessful. At low temperature the expected changes in J_{AB}, in fact, occurred; high values increased and low values decreased. Chemical shifts were calculated by standard methods for AB spectra. The ^{13}C NMR spectra were also determined by standard techniques; both coupled and decoupled spectra were run, and peak identification utilized the expected changes in ^1J with electronegativity. The concentration of solution was from 0.1 to 0.3 g/3.0 mL of $CDCl_3$. In a typical run, 5K transients were collected by using an acquisition time of 0.4 s for a spectral width of 5 cm^{-1}, a pulse width of 30 μs (tip angle ~50°), and a 1.5-cm^{-1} bandwidth for noise decoupling of protons at 7-W high power decoupler setting. The chemical shifts were calculated from the center line of the $CDCl_3$ signal which was taken at 76.9 ppm from Me_4Si.

The infrared spectra were taken on a Perkin-Elmer 621 instrument. Methylene chloride was used as solvent, as coupling constants in the NMR were similar to those found in $CDCl_3$ solutions, but CH_2Cl_2 was more convenient for IR purposes. The solvent was dried by distilling it twice from P_2O_5 and collecting the distillate in a dried container which was stored in a desiccator. Concentrations of 4 mg/mL and 1 mg/mL were used. In some cases the concentration was further decreased to see if the OH absorption was concentration dependent. New 1-mm sodium chloride cells were used, and the ordinate expansion mode of operation of the instrument was necessary at the lower concentrations.

Acknowledgment. Partial funds for the purchase of the NMR instrument were provided by NSF Grant GP 10293, which is gratefully acknowledged.

Registry No. **3**, 73069-77-9; **3**, trimethylsilyl derivative, 73069-78-0; **4**, 73069-79-1; **5**, 73069-80-4; **6**, 73089-59-5; **7**, 73089-60-8; **8**, 73089-61-9; **8**, trimethylsilyl derivative, 73069-81-5; **9**, 73069-82-6; **10**, 73049-15-7; **10**, trimethylsilyl derivative, 73069-85-9; **11**, 73069-83-7; **12**, 73069-84-8; 3,4-diphenyl-3-buten-2-one, 1722-69-6; *p*-thiocresol, 106-45-6.