1004 *J. Org. Chem.* 1981, *46*, 1004–1009

Conformational Preferences of Tetrasubstituted Ethanes. Steric Perturbations in Sulfones vs. Sulfoxides

Roberta O. Day, Charles A. Kingsbury, and Victor W. Day*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

Received May 29, 1979

Solid-state structures have been determined for *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol and *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol by using single-crystal X-ray diffraction techniques. The two molecules crystallize isomorphously in the centrosymmetric monoclinic space group $P2_1/n$ with four molecules per unit cell. The lattice constants are: $a = 10.714$ (1), $b = 20.690$ (3), $c = 9.414$ (1) Å and $\beta = 92.69$ (1)° for the sulfoxide and $a = 10.879$ (1), $b = 20.834$ (3), $c = 9.329$ (1) Å and $\beta = 92.74$ (1)° for the sulfone. The structural parameters for the threo sulfoxide have been refined (anisotropically for S, O, and C; isotropically for H) by empirically weighted full-matrix least-squares techniques to $R_1 = 0.045$ and $R_2 = 0.049$ using 2041 independent diffractometer-recorded (graphite-monochromated Mo K$\bar{\alpha}$ radiation with full (0.90° wide) ω scans) reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 50.7°$ and $I > 3\sigma(I)$. Similar refinements for the threo sulfone gave $R_1 = 0.053$ and $R_2 = 0.054$ for 2866 independent diffractometer-recorded (Nb-filtered Mo K$\bar{\alpha}$ radiation with θ–2θ scans) reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 55°$ and $I > 2\sigma(I)$. Crystals of both molecules contain intermolecular hydrogen bonds between the alcoholic proton and the (common) sulfoxide oxygen atom of a symmetry-related molecule. Small but statistically significant ($>5\sigma$) differences exist between the two molecules for only three bond lengths and two bond angles; all but one of these differences appear to result from the sulfur atom in the sulfoxide keeping its unshared electron pair in the more stable s (relative to p) orbital. The remaining bond angle difference and the significant differences in three of the six dihedral angles involving the ethanic bonds in the two molecules seem to be sterically induced by the incorporation of the (second) sulfone oxygen atom. Intramolecular steric crowding is responsible for the significant deviations of certain bond angles from idealized sp^2- or sp^3-hybridized values observed in both compounds. The solution spectra are shown to be consistent with conformational populations dictated by the interplay of intramolecular hydrogen-bonding effects and minimization of steric repulsions between bulky groups, along the lines suggested by J. L. Mateos and D. J. Cram (*J. Am. Chem. Soc.*, 81, 2756 (1959)).

Introduction

Whereas the ability of X-ray crystallographic structural analyses to provide highly detailed information concerning preferred molecular conformations in the solid state is well-known, the ability of crystal-packing forces to produce distorted molecular conformations is equally well-known.[1] It is perhaps for this reason that relatively few sterically hindered tetrasubstituted ethane molecules like 3–11 in ref 2 have been studied crystallographically, since crystal-packing forces could have a pronounced effect on their molecular conformation. Ideally, one would like to apply the full power of X-ray structural techniques to systems in the absence of crystal-packing forces. Since this is not possible, the next best thing would be to perform solid-state conformational studies for species which can be made to experience the same crystal-packing forces before and after chemical (and structural) modification. This criterion would be met if the two molecules crystallized isomorphously, and studies of such species, in addition to identifying specific solid-state species, provide a basis for predicting molecular conformations by assessing the relative importance of the various types of stereochemical adjustment in determining preferred minimum-energy conformations.

Of the several types of geometrical alteration available to a given molecule for minimizing sterically unfavorable intramolecular interactions, rotations about single bonds and bond angle deformations (especially for those bond angles involving ethanic carbon atoms in tetrasubstituted ethanic moieties) are expected to make the most significant contributions.[3] Sterically induced bond length alterations are expected to be much less significant for the present systems since they represent a considerably higher energy process.[3] Although a number of examples of substantially elongated bonds between two tetracoordinate carbon atoms are known, all of the very long C–C bonds (>1.611 Å) are bridged by at least one other bond[4] and therefore energetically quite different from the present systems.

High-precision X-ray structural analyses were performed for single crystals of *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (**8**) and *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (**10**) in order to provide this type of minimum-energy information for the present systems while simultaneously giving valuable data for comparison with solution conformations of these[2] and other species.[5] Since **8** and **10** crystallize isomorphously, they should experience nearly identical crystal-packing forces. Their crystallographic analyses therefore also provide a unique opportunity for rigorously assessing (in the solid state) the structural differences between sulfoxides and sulfones. Under these circumstances, any observed differences in structural parameters between the two should be a direct result of steric or electronic differences produced by the presence of the second sulfone oxygen atom (O_3 of Figure 1) in **10** but not in **8**.

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[1] Selected examples where crystal-packing forces are believed to produce distorted solid-state molecular conformations include: (a) P. Luger, G. Kothe, and H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, 16, 52 (1977), where a highly strained carbohydrate conformation is present in the solid state but almost certainly not in solution; (b) S. Perez and F. Brisse, *Can. J. Chem.*, **53**, 3551 (1975), where a dramatic conformational change in the ethanic skeleton results when the molecule is modified at a site distant to the ethanic bond; and (c) T. N. Margulis, *J. Am. Chem. Soc.*, **93**, 2193 (1971), where a cyclobutane derivative was shown to be planar or puckered, depending on the crystalline state. Conformation differences are also common between molecules in the gaseous and liquid states: (d) R. J. Abraham and T. M. Siverns, *J. Chem. Soc., Perkin Trans. 2*, 1587 (1972). Thus, factors other than nonbonded intramolecular interactions may dramatically effect the conformation of a molecule in a given physical state.

[2] C. A. Kingsbury, V. W. Day, and R. O. Day, *J. Org. Chem.*, **45**, 5255 (1980).

[3] E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962.

[4] W. D. Hounshell, D. A. Dougherty, J. P. Hummel, and K. Mislow, *J. Am. Chem. Soc.*, **99**, 1916 (1977), and references cited therein.

[5] (a) V. W. Day, R. O. Day, and C. A. Kingsbury, *Tetrahedron Lett.*, 3041 (1976); (b) S. Brownstein, J. Dunogues, D. Lindsay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 2073 (1977); (c) D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *ibid.*, **99**, 6149 (1977).

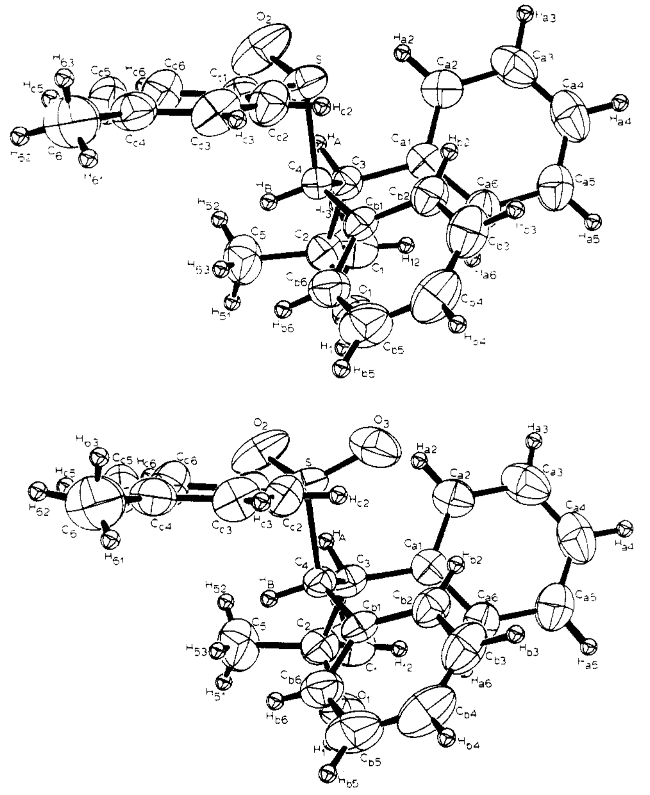

Figure 1. Perspective ORTEP drawings showing the solid-state molecular structures and conformations for (a) (top) *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (8) and (b) (bottom) *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (10). All atoms except hydrogen are represented by an (50% probability) ellipsoid having the shape, orientation, and relative size consistent with the refined anisotropic thermal parameters listed in Table II.[6] Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity. Both molecules are oriented identically and are viewed nearly parallel to the C_3–C_4 ethanic bond.

Results and Discussion

Solid-State Structures of Threo Sulfoxide 8 and Threo Sulfone 10. Final atomic coordinates and thermal parameters for the X-ray structural analyses of crystalline *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (8) and *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (10) are presented in Tables I and II.[6] The numbering scheme used to designate atoms of 8 and 10 is as follows. When more than one atom of a given element occurs within the same molecule, these atoms are distinguished from one another by a set of subscripts unique to their atomic symbol. Carbon atoms of the 2-butanol backbone are subscripted numerically according to their position in the alkyl chain. Atoms of the 2-methyl substituent are designated by a numerical subscript 5 and those of the tolyl methyl group by a subscript 6. Atoms of the 3- and 4-phenyl substituents carry literal subscripts a and b, respectively, as well as numerical subscripts to distinguish between atoms of the same element in the same substituent. Similarly, atoms of the six-membered ring of the 4-tolyl substituent have a literal subscript c and numerical subscripts. Atoms of the 2-hydroxyl group have a numerical subscript 1. O_2 is the sulfoxide oxygen atom common to 8 and 10. With the exception of the two ethanic hydrogen atoms which are designated H_A and H_B (bonded to C_3 and C_4, respectively), each symbol for a hydrogen atom carries the same subscript(s) as the nonhydrogen atom to which it is covalently bonded. In addition, methyl hydrogens carry a third (numerical) subscript to distinguish between hydrogens on the same carbon atom.

Identically oriented perspective models which illustrate this naming scheme and represent the contents of the asymmetric units of sulfoxide 8 and sulfone 10 specified by the atomic coordinates of Table I are shown in Figure 1; each nonhydrogen atom is represented by an ellipsoid having the shape, orientation, and relative size consistent with the thermal parameters listed in Table II[6] (hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion). Both molecules exist in the T_{GI} conformer of Scheme I in ref 2 and have oxygen atom O_2 (Figure 1) *intermolecularly* hydrogen bonded to the hydroxyl group of a symmetry-related ($^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$) molecule in the lattice. Values of 2.740 (4) Å and 2.796 (4) Å for the $O_2 \cdots O_1'$ distance and 171 (4)° and 176 (4)° for the $O_2 \cdots H_1'$—O_1' angle were observed for 8 and 10, respectively.

Detailed comparisons of covalent bond lengths and angles involving nonhydrogen atoms in 8 and 10 are presented in Tables III and IV, respectively. Corresponding comparisons of covalent bond lengths and angles involving hydrogen atoms are presented in Tables VI and VII, respectively.[6] Short nonbonded intramolecular contacts for 8 and 10 are listed in Table V. Newman projections, labeled with dihedral angles involving the ethanic C_3–C_4 bonds of 8 and 10, are shown in Figure 2.

The data in Tables III and IV reveal normal bond lengths in both compounds for bonds not involving sulfur but several bond angles which deviate significantly from their idealized sp^2- and sp^3-hybridized values of 120.0° and 109.5°, respectively.

Lengths for C–C bonds of a given type do not vary significantly in either compound. Averaged values of 1.537 (5, 15, 19) Å[7] and 1.540 (6, 11, 15) Å[7] were observed for the sp^3–sp^3 C–C bonds in 8 and 10, respectively; similarly averaged values of 1.514 (5, 2, 3) Å and 1.510 (5, 6, 9) Å were determined for the sp^2–sp^3 C–C bonds. These are in fact very nearly the bond lengths (1.544 Å for sp^3–sp^3 C–C and 1.515 Å for sp^2–sp^3 C–C bonds) which one obtains by summing the appropriate single bond radii for sp^2- (0.743 Å)[8] and sp^3-hybridized (0.772 Å)[9] carbon atoms. Averaged phenyl C–C bond lengths of 1.378 (5, 6, 20) Å in 8 and 1.379 (6, 8, 17) Å in 10 are in close agreement with the generally accepted value of 1.39 Å. The 25 independent C–H bonds each in 8 and 10 have averaged values of 0.93 (4, 3, 12) Å and 0.94 (4, 3, 10) Å, respectively, which are in excellent agreement with values determined for high-precision X-ray studies of compounds containing similar bonds.[10] Values of 1.421 (4) Å and 1.424 (4) Å for the C_2–O_1 bonds as well as 0.74 (4) Å and 0.78 (4) Å for the O_1–H_1 bonds in 8 and 10, respectively, are typical X-ray values for single bonds from oxygen to carbon and hydrogen, respectively.[11] The 0.032 Å elongation of the S–O_2 bond in 10 relative to the

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[6] See paragraph at end of paper regarding Supplementay Material.

[7] The first number in parentheses following an averaged value is the root-mean-square value of the estimated standard deviation of a single datum. The second and third numbers, when given, represent the mean and maximum deviations from the averaged value, respectively.

[8] D. R. Lide, Jr., *Tetrahedron*, 17, 125 (1962).

[9] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960, pp 224–8.

[10] (a) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973); (b) F. A. Cotton, V. W. Day, E. E. Hazen, Jr., and S. Larsen, *J. Am. Chem. Soc.*, **95**, 4834 (1973); (c) F. A. Cotton, V. W. Day, E. E. Hazen, Jr., S. Larsen, and S. T. K. Wong, *ibid.*, **96**, 4471 (1974); (d) H. E. Baumgarten, D. G. McMahan, V. J. Elia, B. I. Gold, V. W. Day, and R. O. Day, *J. Org. Chem.*, 41, 3798 (1976).

[11] "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, p 276.

Table III. Covalent Bond Lengths (Å) for Nonhydrogen Atoms in Crystalline *threo*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (10) and *threo*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (8)[a]

type[b]	sulfone (10)	sulfoxide (8)	type[b]	sulfone (10)	sulfoxide (8)
S-O_2	1.444 (3)	1.471 (3)	C_{a1}-C_{a2}	1.380 (4)	1.385 (5)
S-O_3	1.412 (3)	*d*	C_{a1}-C_{a6}	1.387 (4)	1.394 (5)
S-C_4	1.817 (3)	1.848 (3)	C_{a2}-C_{a3}	1.380 (4)	1.389 (6)
S-C_{c1}	1.762 (3)	1.790 (4)	C_{a3}-C_{a4}	1.358 (6)	1.366 (6)
C_2-O_1	1.421 (4)	1.424 (4)	C_{a4}-C_{a5}	1.370 (6)	1.372 (6)
C_1-C_2	1.526 (5)	1.533 (6)	C_{a5}-C_{a6}	1.381 (5)	1.385 (5)
C_2-C_3	1.549 (4)	1.547 (5)	C_{b1}-C_{b2}	1.386 (4)	1.391 (5)
C_2-C_5	1.518 (6)	1.525 (6)	C_{b1}-C_{b6}	1.384 (4)	1.384 (5)
C_3-C_4	1.556 (4)	1.555 (5)	C_{b2}-C_{b3}	1.378 (5)	1.380 (5)
sp^3-sp^3	av 1.537 (5, 15, 19)[c]	1.540 (6, 11, 15)[c]	C_{b3}-C_{b4}	1.361 (6)	1.362 (6)
C_3-C_{a1}	1.514 (4)	1.507 (5)	C_{b4}-C_{b5}	1.376 (6)	1.383 (7)
C_4-C_{b1}	1.516 (4)	1.519 (5)	C_{b5}-C_{b6}	1.379 (5)	1.381 (6)
C_6-C_{c4}	1.511 (6)	1.503 (6)	C_{c1}-C_{c2}	1.383 (4)	1.372 (5)
sp^2-sp^3	av 1.514 (5, 2, 3)[c]	1.510 (5, 6, 9)[c]	C_{c1}-C_{c6}	1.381 (5)	1.368 (5)
			C_{c2}-C_{c3}	1.369 (5)	1.384 (6)
			C_{c3}-C_{c4}	1.383 (5)	1.376 (6)
			C_{c4}-C_{c5}	1.380 (5)	1.385 (6)
			C_{c5}-C_{c6}	1.372 (5)	1.371 (5)
			phenyl C-C	av 1.378 (5, 6, 20)[c]	1.379 (6, 8, 17)[c]

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms labeled in agreement with Figures 1 and 2. [c] The first number in parentheses following an averaged value is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. [d] Atom O_3 is not present in sulfoxide 8.

Table IV. Bond Angles (deg) for Nonhydrogen Atoms in Crystalline *threo*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (10) and *threo*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (8)[a]

type[b]	sulfone (10)	sulfoxide (8)	type[b]	sulfone (10)	sulfoxide (8)
O_2SO_3	117.4 (2)	*c*	$C_{a6}C_{a1}C_{a2}$	117.4 (3)	117.4 (3)
O_3SC_4	112.3 (2)	*c*	$C_{a1}C_{a2}C_{a3}$	121.3 (4)	121.2 (4)
O_3SC_{c1}	109.1 (1)	*c*	$C_{a2}C_{a3}C_{a4}$	120.5 (4)	120.3 (4)
O_2SC_4	105.3 (1)	104.9 (2)	$C_{a3}C_{a4}C_{a5}$	119.5 (4)	119.7 (4)
O_2SC_{c1}	107.5 (2)	106.9 (2)	$C_{a4}C_{a5}C_{a6}$	120.4 (4)	120.2 (4)
C_4SC_{c1}	104.5 (1)	98.8 (2)	$C_{a5}C_{a6}C_{a1}$	121.0 (4)	121.1 (4)
$C_1C_2C_3$	110.2 (3)	109.5 (3)	$C_{b6}C_{b1}C_{b2}$	118.8 (3)	118.6 (3)
$C_1C_2C_5$	108.2 (3)	108.1 (4)	$C_{b1}C_{b2}C_{b3}$	120.3 (4)	120.5 (4)
$C_3C_2C_5$	111.2 (3)	111.6 (3)	$C_{b2}C_{b3}C_{b4}$	120.5 (4)	120.6 (4)
$O_1C_2C_1$	110.7 (3)	110.5 (3)	$C_{b3}C_{b4}C_{b5}$	120.0 (4)	119.5 (4)
$O_1C_2C_3$	106.8 (2)	107.8 (3)	$C_{b4}C_{b5}C_{b6}$	120.1 (4)	120.4 (4)
$O_1C_2C_5$	109.7 (3)	109.3 (4)	$C_{b5}C_{b6}C_{b1}$	120.4 (4)	120.3 (4)
$C_2C_3C_4$	111.3 (2)	112.1 (3)	$C_{c6}C_{c1}C_{c2}$	120.0 (3)	119.8 (4)
SC_4C_3	110.3 (2)	107.2 (2)	$C_{c1}C_{c2}C_{c3}$	119.6 (3)	119.4 (4)
SC_4C_{b1}	108.3 (2)	107.9 (2)	$C_{c2}C_{c3}C_{c4}$	121.0 (3)	121.4 (4)
$C_2C_3C_{a1}$	115.3 (2)	115.7 (3)	$C_{c3}C_{c4}C_{c5}$	118.7 (3)	118.1 (4)
$C_4C_3C_{a1}$	114.2 (2)	113.3 (3)	$C_{c4}C_{c5}C_{c6}$	120.9 (4)	120.7 (4)
$C_3C_4C_{b1}$	121.1 (2)	120.6 (3)	$C_{c5}C_{c6}C_{c1}$	119.7 (3)	120.7 (4)
$C_3C_{a1}C_{a2}$	119.6 (3)	119.7 (3)	$C_6C_{c4}C_{c3}$	121.6 (4)	121.1 (4)
$C_3C_{a1}C_{a6}$	123.0 (3)	122.8 (3)	$C_6C_{c4}C_{c5}$	119.6 (4)	120.9 (4)
			$SC_{c1}C_{c2}$	120.3 (2)	119.5 (3)
			$SC_{c1}C_{c6}$	119.7 (3)	120.7 (3)
			$C_4C_{b1}C_{b2}$	123.0 (3)	121.9 (3)
			$C_4C_{b1}C_{b6}$	118.2 (3)	119.2 (3)

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms labeled in agreement with Figures 1 and 2. [c] Atom O_3 is not present in sulfoxide 8.

S–O_3 bond is presumably due to the participation of O_2 in a solid-state intermolecular hydrogen bond with the hydroxylic proton of a symmetry-related molecule. The atoms comprising each of the following groupings are coplanar to within 0.01 Å in both molecules: C_{a1}, C_{a2}, C_{a3}, C_{a4}, C_{a5}, and C_{a6}; C_{b1}, C_{b2}, C_{b3}, C_{b4}, C_{b5}, and C_{b6}; and C_{c1}, C_{c2}, C_{c3}, C_{c4}, C_{c5}, and C_{c6}.

The similarity of equivalent bond lengths and angles for 8 and 10 is rather striking. Small but statistically significant ($>5\sigma$) differences exist between the two molecules for only three bond lengths and two bond angles, all of which involve the sulfur atom; three of the six dihedral angles involving the ethanic bond have significant differences. Only the dihedral angle differences and one of the bond angle alterations appear to be sterically induced; the remaining differences appear to be electronic in nature. The ~0.029-Å elongations of the S–O_2, S–C_4, and S–C_{c1} bonds as well as the 5.7° contraction of the C_4–S–C_{c1} angle in 8 relative to 10 are all presumably the result of the tendency for the sulfur atom in 8 to keep its unshared electron pair in the more stable s (relative to p) orbital, thereby reducing the amount of s character in the sulfur bond orbitals and producing weaker (and longer) S–X (where X = C or O) bonds and smaller X–S–X′ bond angles in 8 relative to 10. The significant deviations of certain bond angles from idealized sp^2- or sp^3-hybridized values observed in both compounds are presumably the result of steric crowding within the molecules and will be discussed

Table V. Short Nonbonded Intramolecular Contacts (Å) in Crystalline *threo*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (10) and *threo*-2-Methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (8)[a]

type[b]	sulfone (10)	sulfoxide (8)	type[b]	sulfone (10)	sulfoxide (8)
$S\cdots C_{b2}$	3.253 (3)	3.138 (4)	$O_1\cdots H_{a6}$	2.40 (3)	2.41 (3)
$S\cdots C_{a1}$	3.419 (3)	3.307 (3)	$O_2\cdots H_A$	2.38 (3)	2.35 (3)
$S\cdots C_{a2}$	3.634 (3)	3.452 (4)	$O_2\cdots H_{c6}$	2.47 (3)	2.59 (3)
$O_1\cdots C_4$	2.867 (4)	2.911 (4)	$O_3\cdots H_{b2}$	2.53 (3)	*c*
$O_1\cdots C_{a6}$	3.040 (4)	3.036 (5)	$C_1\cdots H_1$	2.47 (4)	2.50 (4)
$O_1\ldots C_{a1}$	3.087 (4)	3.091 (4)	$C_1\cdots H_A$	2.72 (3)	2.72 (3)
$O_1\cdots C_{b1}$	3.092 (3)	3.108 (4)	$C_2\cdots H_B$	2.57 (3)	2.61 (3)
$O_2\cdots C_{c6}$	2.917 (5)	2.948 (5)	$C_2\cdots H_{a6}$	2.87 (3)	2.90 (3)
$O_2\cdots C_3$	2.975 (4)	2.960 (4)	$C_4\cdots H_{53}$	2.75 (5)	2.80 (5)
$O_3\cdots C_{c2}$	3.006 (4)	*c*	$C_5\cdots H_1$	2.51 (4)	2.48 (4)
$O_3\cdots C_{b2}$	3.059 (4)	*c*	$C_5\cdots H_A$	2.57 (3)	2.61 (3)
$C_1\cdots C_{a1}$	2.933 (5)	2.936 (6)	$C_5\cdots H_B$	2.56 (3)	2.62 (3)
$C_1\cdots C_{a6}$	3.312 (6)	3.339 (6)	$C_{a1}\cdots H_{12}$	2.64 (4)	2.61 (4)
$C_2\cdots C_{a6}$	3.117 (5)	3.122 (5)	$C_{a1}\cdots H_{b2}$	2.83 (3)	2.80 (3)
$C_3\cdots C_{b2}$	3.393 (4)	3.390 (5)	$C_{a2}\cdots H_A$	2.50 (3)	2.49 (3)
$C_4\cdots C_5$	3.046 (5)	3.062 (6)	$C_{a6}\cdots H_{12}$	2.71 (5)	2.71 (4)
$C_{a1}\cdots C_{b1}$	3.153 (4)	3.136 (5)	$C_{a6}\cdots H_{b2}$	2.91 (3)	2.86 (3)
$C_{a1}\cdots C_{b2}$	3.245 (5)	3.231 (5)	$C_{b6}\cdots H_B$	2.49 (3)	2.50 (3)
$C_{a6}\cdots C_{b2}$	3.198 (5)	3.166 (5)	$C_{c1}\cdots H_B$	2.80 (3)	2.70 (3)
$C_{a6}\cdots C_{b1}$	3.385 (4)	3.354 (5)	$H_A\cdots H_{a2}$	2.29 (4)	2.26 (4)
$C_{b1}\cdots C_{c1}$	3.196 (4)	3.160 (5)	$H_A\cdots H_B$	2.31 (4)	2.35 (4)
$C_{b1}\cdots C_{c2}$	3.369 (4)	3.309 (5)	$H_A\cdots H_{52}$	2.35 (6)	2.45 (6)
$S\cdots H_A$	2.58 (3)	2.63 (3)	$H_B\cdots H_{53}$	2.04 (6)	2.14 (5)
$S\cdots H_{b2}$	3.07 (3)	2.89 (3)	$H_B\cdots H_{b6}$	2.23 (4)	2.31 (4)
			$H_{11}\cdots H_{51}$	2.35 (5)	2.38 (5)

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms labeled in agreement with Figures 1 and 2. [c] Atom O_3 is not present in sulfoxide 8.

below. With the exception of the intermolecular hydrogen bond between O_2 and a symmetry-related H_1–O_1 group, no intermolecular contact distances are less than the sum of their respective van der Waals radii.[12]

As anticipated, both 8 and 10 alleviate seriously short nonbonded intramolecular contacts between the bulky ethanic substituents primarily through bond angle deformations and rotation about the C_3–C_4 bond from the (idealized) staggered conformation. The dihedral angles shown in Figure 2 are, however, somewhat surprising at first, with values of ~49° and ~72° for the C_{a1}–C_3–C_4–C_{b1} and H_A–C_3–C_4–H_B angles, respectively, in both compounds. The remaining dihedral angles between vicinal bulky substituents (C_{a1}–C_3–C_4–S and C_2–C_3–C_4–C_{b1}) have the expected values of >60° with the largest (~84°) angle occurring between the bulkiest (dimethylhydroxycarbinyl) group and its vicinal phenyl (Ph_b) substituent. The 7.3° expansion of the C_{a1}–C_3–C_4–S dihedral angle, the 3.1° expansion of the C_3–C_4–S bond angle, and increases in the $S\cdots C_{a1}$ and $S\cdots C_{b2}$ separations in 10 relative to 8 are all due to the presence of O_3 in 10 but not in 8. O_3 makes normal van der Waals[12] contacts with C_{a2} and C_{b2}.

The interiors of both molecules appear to be quite congested; the C_2–C_3–C_4, C_4–C_3–C_{a1}, and C_3–C_4–C_{b1} angles are all significantly (by as much as 11.6°) larger than the idealized sp^3-hybridized value. It is perhaps also noteworthy that a slight amount of sterically induced bond elongation has occurred for the C_3–C_4 bond; it is the longest sp^3–sp^3 C–C bond in both compounds (1.555 (5) Å in 8 and 1.556 (4) Å in 10). The fact that seriously short (>0.20 Å less than the sum of their respective van der Waals radii) nonbonded intramolecular contacts exist for only eight pairs of nonhydrogen atoms in 8 and/or 10 clearly indicates that the T_{G1} conformer with the observed bond angles and ethanic dihedral angles has achieved a reasonably comfortable fit of the four bulky substituents attached to the ethanic bond. Furthermore, of these eight short contacts ($S\cdots C_{b2}$, $S\cdots C_{a1}$, $C_1\cdots C_{a1}$, $C_2\cdots C_{a6}$, $C_4\cdots C_5$, $C_{a1}\cdots C_{b1}$, $C_{a6}\cdots C_{b2}$, and $C_{b1}\cdots C_{c1}$), only three involve atoms of a pair of vicinal ethanic substituents. Whereas rotation about the C_3–C_4 bond to give a larger C_{a1}–C_3–C_4–C_{b1} dihedral angle would improve the $C_{a1}\cdots C_{b1}$ and $C_{a6}\cdots C_{b2}$ contacts, it would worsen the $S\cdots C_{a1}$ contact. Significant expansions of the C_3–C_2–C_5 and C_2–C_3–C_{a1} bond angles from the idealized 109.5° value are probably produced by the (short) $C_4\cdots C_5$, $C_1\cdots C_{a1}$, and $C_2\cdots C_{a6}$ contacts. It is also noteworthy that three of the eight short contacts involve atoms of the bulky dimethylhydroxycarbinyl substituents whose observed orientations in 8 and 10 with regard to rotation about the C_2–C_3 bond are clearly dictated by steric factors. The bulkier methyl (relative to hydroxy) groups are directed away from the congested interior of the molecule. Altona showed some years ago that 1,3-interactions involving oxygen are not extremely repulsive.[13]

Structural and Conformational Effects of Second Sulfone Oxygen. The above detailed comparison for the solid-state structures of threo sulfoxide 8 and threo sulfone 10 can be summarized as follows. Small but statistically significant (>5σ) differences exist in the solid state between 8 and 10 for only three bond lengths and two bond angles; all but one of these differences appear to be electronically induced by the sulfoxide sulfur atom in 8 keeping its unshared electron pair in the more stable s (relative to p) orbital. The remaining bond angle difference and the significant differences in three of the six dihedral angles involving the ethanic C_3–C_4 bonds of 8 and 10 seem to be sterically induced by the incorporation of the (second) sulfone oxygen atom (O_3) in 10. Significant deviations of several bond angles from idealized sp^2- or sp^3-hybridized values in both compounds can be explained in terms of intramolecular steric crowding.

Rationale for the Solution and Solid-State Conformations of 3–11. Having shown that bond length and

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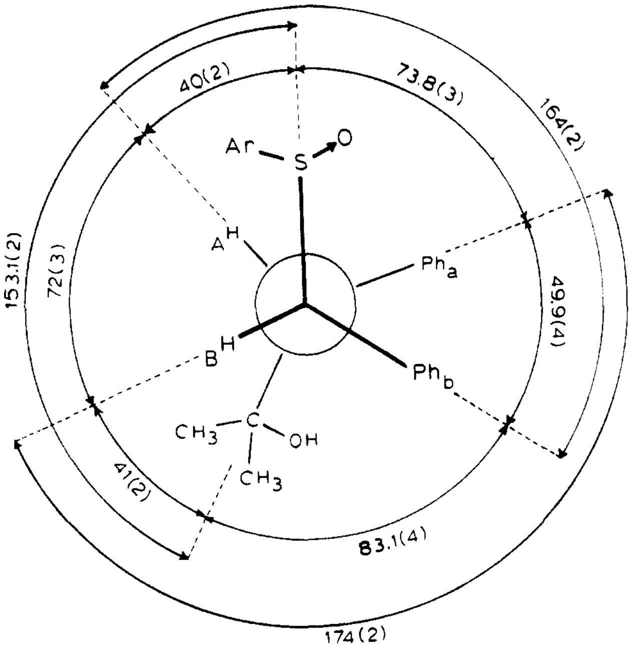
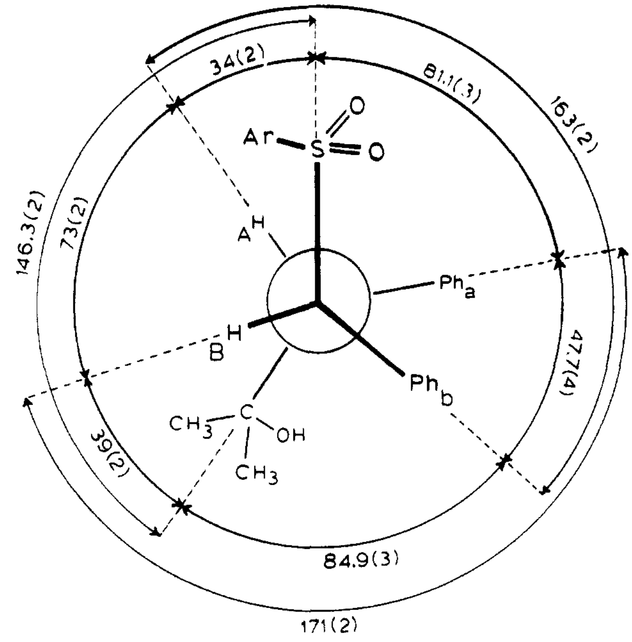
(12) Reference 9, p 260.

(13) C. Altona and H. Hirschmann, *Tetrahedron*, 26, 2173 (1970), and references cited therein.



8

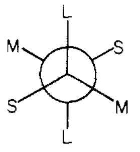


10

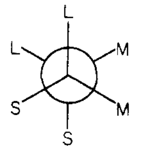
Figure 2. Newman projections showing the various dihedral angles involving the ethanic C_3–C_4 bonds in (a) (top) threo sulfoxide 8 and (b) (bottom) threo sulfone 10. The number in parentheses following each dihedral angle value is the estimated standard deviation in that value.

angle differences between 8 and 10 are primarily electronic in nature while the conformational differences are sterically induced, we would now like to analyze the spectroscopic data for the entire series (3–11) of sulfides, sulfoxides, and sulfones[2] as well as the solid-state data for 8 and 10 in terms of current conformational theories. In 1959, Mateos and Cram postulated conformational preferences to be expected for diastereomeric disubstituted ethanes, based on steric interactions of large (L), medium (M), and small (S) groups.[14] Later, Zimmerman et al. termed such diastereomers erythro-s, etc., indicating that the classification was based on the size of groups.[15] Such an analysis is, however, not valid under all conditions for molecules such as 3–11 which are capable of forming intramolecular hydrogen bonds. Clearly, intramolecular hydrogen bonding affects the conformational preferences of sulfides 3 and 4 and sulfoxides 6 and 8 in solvents such as $CDCl_3$ and benzene. A change of solvent to Me_2SO for 3, 4, and 6 disrupts the intramolecular hydrogen bond to a greater or lesser degree, depending on the compound, and produces a change in conformation. However, the ability of steric (or other) factors to outweigh the stability afforded by intramolecular hydrogen bond formation is indicated by the absence of such interactions in sulfoxide 5 and sulfone 9. We will therefore restrict our conformational analyses for 3–10 to those systems where intramolecular hydrogen-bonding effects are minimized (e.g., the solid state,[1] in solution with Me_2SO as solvent, or where trimethylsilyl (Me_3Si) deviatives have been made).

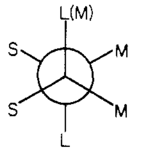
Mateos and Cram[14] predicted that the erythro-s conformer of greatest stability would be 12 (analogous to E_T of Scheme I in ref 2). Subsequent work[16] indeed showed many cases in which this prediction was upheld, including sulfoxide 5 and sulfone 9 of the present study. In 12, L···L contacts, which would result in strong steric interference, are absent. Only two L···M contacts exist, each set being separated by a small group. The substituents in sulfones 9 and 10 can clearly be distinguished sizewise with $[(CH_3)_2(OH)C-]$ and $[CH_3C_6H_4SO_2-]$ being L groups, phenyls being M groups, and hydrogens being S groups. Such distinctions are less clear-cut for the sulfoxides and sulfides. Although the crystallographic data presented above for 8 and 10 clearly indicate that the sulfoxide substituent is less bulky than the corresponding sulfone substituent, the extent to which the effective size is decreased in a given molecule depends heavily on the chirality of all three (C_3, C_4, and S) optical centers. One sulfoxide configuration may represent a "large" substituent while another represents a more "medium-sized" one.



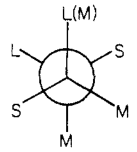
12 (E_T)



13 (E_G)



14 (T_{G_1})



15 (T_T)

For the threo-s diastereomers, Mateos and Cram predicted that 14 (T_{G1} of Scheme I, ref 2) would be somewhat more stable than 15 (T_T of Scheme I, ref 2), which would be substantially more stable than the third possible conformer (T_{G2} of Scheme I, ref 2). However, exceptions to this order of stability were considered quite possible, and subsequent work has shown cases in which 14 is preferred,[17] as well as cases in which 15 is preferred.[18] In a given test case, reliable predictions of conformation cannot be made with certainty. However, in the case of sulfone 10 and the Me_3Si derivative of 8, the L···L contact between the $Ar-SO_n-$ and $[(CH_3)_2(OR)C-]$ groups appears to be prohibitive and 14 (T_{G1}) is favored over 15 (T_T). Thus the

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[14] J. L. Mateos, and D. J. Cram, *J. Am. Chem. Soc.*, 81, 2756 (1959).

[15] H. E. Zimmerman and W.-H. Chang, *J. Am. Chem. Soc.*, 81, 3634 (1959).

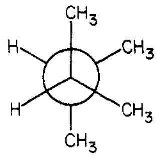
[16] D. C. Best and C. A. Kingsbury, *Org. Chem.*, 32, 6 (1967), and many similar papers.

[17] D. C. Best and C. A. Kingsbury, *J. Org. Chem.*, 33, 3252 (1968).

[18] R. A. Auerbach and C. A. Kingsbury, *Tetrahedron*, 29, 1457 (1973).

L···L interaction of **15** (in **10**) is formally replaced by a L···M interaction (in **7**), which is no longer prohibitive, and **15** (T_T) becomes preferred. Many diastereomers with vicinal phenyl groups prefer conformers such as **15** (T_T) in which vicinal hydrogens are trans and in which the total number of contacts between sizable groups is minimized.[5a]

Unfortunately the L, M, S analysis is at best an approximation of the interactions for various groups and can therefore only be used to give qualitative conformational predictions. Furthermore, this approach focuses attention to the states of internal rotation typified by conformers **12**–**15**, and without an absolute method of structure determination such as X-ray crystallography, the relative orientations of the L, M, and S groups will not be accurately known. Although the crystallographic structure of **10** is consistent with the L, M, S analysis, the highly skewed dihedral angles are in marked contrast to the common assumption of 60° dihedral angles and suggest that a simple analysis based on the size of groups may not always be valid. Allinger et al. have shown that variations in bond angles are often at least as important a factor as the state of internal rotation in determining molecular conformation; these may in fact necessitate a seemingly unstable conformer, such as **16**.[5b,19] The crystallographic structures of **8** and **10** also clearly demonstrate the importance of bond angle variations. Thus, the Ph groups (considered by Cram and Mateos as L groups) appear to lie very close to one another in Figure 2. However, these Ph groups experience only normal van der Waals contacts due to the spreading of the C–C–Ph bond angles (to as much as 120°!). Crystallographic studies designed to assess the relative importance of such bond angle variations and size considerations are under way.



16

Experimental Section

Crystallographic Analyses. Large well-shaped prismatic single crystals of *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol, **8** ($C_{24}H_{26}O_2S$, mol wt 378.55), and *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol, **10** ($C_{24}H_{26}O_3S$, mol wt 394.55), suitable for X-ray diffraction studies were grown from 95% ethanol. Single crystals of both compounds were morphologically indistinguishable and an admixture of **10** did not depress the melting point of **8**. Both compounds crystallize in the centrosymmetric monoclinic space group $P2_1/n$ (an alternate setting of $P2_1/c$-C_{2h}^5, No. 14)[20,21] with $a = 10.714$ (1) Å, $b = 20.690$ (3) Å, $c = 9.414$ (1) Å, $\beta = 92.69$ (1)°, and $Z = 4$ [$d_{calcd} = 1.206$ g cm^{-3}, $d_{measd} = 1.191$ g cm^{-3}, and μ_a(Mo K$\bar{\alpha}$)[22] = 0.17 mm^{-1}] for **8** and $a = 10.879$ (1) Å, $b = 20.834$ (3) Å, $c = 9.329$ (1) Å, $\beta = 92.74$ (1)°, and $Z = 4$ [$d_{calcd} = 1.241$ g cm^{-3}, $d_{measd} = 1.235$ g cm^{-3}, and μ_a(Mo K$\bar{\alpha}$)[22] = 0.17 mm^{-1}] for **10**. Intensity measurements were made on a computer-controlled Syntex $P\bar{1}$ autodiffractometer for spherical specimens of both compounds which had diameters of ~0.52 mm ($\mu r = 0.05$). Measurements for **8** which utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (0.90° wide) ω scans gave a total of 3814 independent reflections having $2\theta_{MoK\bar{\alpha}} < 50.7°$. Measurements for **10** utilized Nb-filtered Mo K$\bar{\alpha}$ radiation, full (≥2° wide) θ–2θ scans, and gave 4884 independent reflections with $2\theta_{MoK\bar{\alpha}} < 55°$. For those reflections of **8** having $2\theta_{MoK\bar{\alpha}} < 43°$, a scanning rate of 3°/min was employed for the scan between ω settings 0.45°, respectively, above and below the calculated K$\bar{\alpha}$ doublet value ($\lambda_{K\bar{\alpha}} = 0.71069$ Å). A scanning rate of 2°/min was used for the remaining reflections of **8**. Each 0.90° scan was divided into 15 equal (time) intervals and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts for reflections of **8**, each lasting for one-fourth the total time used for the net scan ($^{13}/_{15}$th of the total scan time), were measured at ω settings 0.9° above and below the calculated K$\bar{\alpha}$ doublet value for each reflection. A scanning rate of 3°/min was also employed for the scan between 2θ settings 1.0° above and below the calculated Kα doublet values for each reflection of **10**. Background counts for **10**, each lasting for half the total scan time, were taken at both ends of the scan range. Since the absorption of X-rays by a spherical crystal having $\mu r = 0.05$ is virtually independent of scattering angle,[23] the data for neither compound were corrected for absorption.

The nonhydrogen atoms of threo sulfone **10** were located by using direct methods (MULTAN) and difference Fourier techniques, and those of threo sulfoxide **8** were derived from the parameters of **10**. All chemically anticipated hydrogen atoms for both molecules were located from difference Fourier syntheses calculated from the appropriate full-matrix least-squares refined structural model [R_1 (unweighted, based on F) = 0.092 and 0.091 for **8** and **10**, respectively] which incorporated unit-weighting and anisotropic thermal parameters for all nonhydrogen atoms and reflections having $2\theta_{MoK\bar{\alpha}} < 50.7°$ for **8** and $2\theta_{MoK\bar{\alpha}} < 43°$ for **10**. All structure factor calculations for both compounds employed the atomic form factors compiled by Cromer and Mann[24] and an anomalous dispersion correction[25] to the scattering factor of the sulfur atoms. A least-squares refineable extinction correction of the form[26] $1/(1 + gIc)^{1/2}$ was employed for structure factors of **10** but not **8**. The final cycles of empirically weighted full-matrix least-squares refinement which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to values of 0.045 and 0.046 for R_1 and R_2 (weighted, based on F), respectively, for 2041 independent reflections of **8** having $2\theta_{MoK\bar{\alpha}} < 50.7°$ and $I > 3\sigma(I)$.[6] Similar refinement cycles for **10** gave $R_1 = 0.053$ and $R_2 = 0.054$ for 2866 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 2\sigma(I)$.[6]

Acknowledgment. Support of this research by the University of Nebraska Research Council and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank the University of Nebraska Computing Center for a generous grant of computer time. Partial funds for purchase of the XL-100 NMR instrument were provided by NSF Grant GP 10293.

Registry No. 8, 73049-15-7; 10, 73049-15-7.

Supplementary Material Available: A listing of fractional coordinates for all atoms (Table I), anisotropic thermal parameters for nonhydrogen atoms (Table II), bond lengths (Table VI) and angles (Table VII) involving hydrogen atoms, and a detailed description of the experimental conditions for the crystallographic studies of *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfinyl)-2-butanol (**8**) and *threo*-2-methyl-3,4-diphenyl-4-(4-toluenesulfonyl)-2-butanol (**10**) (14 pages). Ordering information is given on any current masthead page. A listing of observed and calculated structure factor amplitudes from the final cycles of least-squares refinement for **8** and **10** may be obtained from the authors.

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(19) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).

(20) "International Tables for X-Ray Crystallography", Vol. I, The Kynoch Press, Birmingham, England, 1969, p 99.

(21) The results of tests for piezoelectricity, made with a Geibe-Schiebe detector, were kindly supplied by Professor J. L. Hoard of Cornell University.

(22) Reference 11, p 166.

(23) "International Tables for X-Ray Crystallography", Vol. II, The Kynoch Press, Birmingham, England, 1967, p 302.

(24) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(25) D. T. Cromer, *Acta Crystallogr., Sect. A*, **18**, 17 (1965).

(26) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).