General Preference for Alkyl/Phenyl Folded Conformations. Relevance of the CH/π[#] and CH/O Interactions to Stereochemistry as Evidenced by Ab Initio MO Calculations

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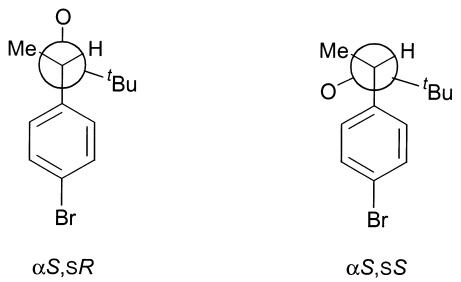
Ab initio MO calculations were carried out, at the MP2/6-311G(d,p)//MP2/6-31G(d) level, to determine the conformational energy of alkyl 1-phenylethyl sulfoxides, $CH_3CH(C_6H_5)$–S(O)–R (R = CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9). In every case, a geometry (rotamer **a**, R/C_6H_5 torsion angle $\phi \sim 60°$) where the alkyl group (R) is *gauche* to the C_6H_5 (Ph) and *anti* to the benzylic methyl group (Me) has been found to be the most stable. Rotamer **b** ($\phi \sim 300°$), where R is flanked by Me and Ph, has been shown the next most stable in every case except for isopropyl and *t*-butyl analogue with the *threo* configuration. The R/Ph *anti* conformation (rotamer **c**: $\phi \sim 180°$) has been found the least stable. Interatomic distances (CH/π as well as CH/O) at the stable geometries are found to be very short. These results are interpreted in the context of the attractive CH/π and CH/O hydrogen bonds and the unfavorable electrostatic interaction between the S–O dipole and the quadrupole of the phenyl group. In view of the above result and of previous findings, the alkyl/phenyl congested folded conformation of aralkyl compounds has been suggested to be a general phenomenon.

More than 25 years have elapsed since one of the authors and co-workers reported on the 'unusual' conformation for a series of *t*-butyl 1-phenylethyl sulfoxides. Thus, in 1974, a X-ray crystallographic study of (α*R*,S*S*/α*S*,S*R*)-*t*-butyl-1-*p*-bromophenylethyl sulfoxide, $CH_3CH(p\text{-}BrC_6H_4)$–S(O)–*t*-$C_4H_9$, demonstrated that the *t*-butyl group was *gauche* to the phenyl (Ph) and *anti* to the benzylic methyl group (Me).[1] Later, its diastereoisomeric congener, (α*R*,S*R*/α*S*,S*S*)-*t*-butyl-1-*p*-bromophenylethyl sulfoxide, was shown to exist in a similar conformation (*t*-Bu/Ph *gauche*) in crystals (Fig. 1)[2].

The solution conformation of these sulfoxides was then studied, by NMR and CD; it was shown that both the diastereoisomers maintained a conformation similar to that in solid. Dipole-moment measurements gave results consistent with this conclusion.[3] The solution conformation of lower alkyl analogues $CH_3CH(C_6H_5)$–S(O)–R (R = CH_3, C_2H_5, *i*-C_3H_7) was examined subsequently.[4] Again, the alkyl group was suggested to be *gauche* to Ph and *anti* to Me in the most preferred conformation (Fig. 2, rotamer **a**: R/Ph torsional angle $\phi \sim 60°$), irrespective of the configuration at the chiral carbon and sulfur atom (*threo* or *erythro*).[5] The second most favorable conformation has been suggested to be R flanked by Ph and Me (rotamer **b**: $\phi \sim 300°$).



αS,sR αS,sS

Fig. 1. X-ray crystallographic results of (α*S*,S*R*)- and (α*S*,S*S*)-*t*-butyl-1-*p*-bromophenylethyl sulfoxides.

The authors suggested that the phenomenon is a consequence of attractive interactions occurring between the alkyl CH and the phenyl π-ring.[6] The weak molecular force, now termed the CH/π interaction,[7] has been recognized as a kind of weak hydrogen bond operating between a soft acid and a soft base. Evidence has since accumulated to indicate that the CH/π interaction plays important roles in the conformational issues of organic compounds.[8]

In a previous paper, we studied the conformation of a series of alkyl 1-phenylethyl ketones, $MeCH(C_6H_5)$–CO–R, by MP2/6-311G(d,p)//MP2/6-31G(d) level calculations.[9] A conformation whereby the group R (CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9) is *gauche* to Ph and *anti* to Me (Fig. 3, rotamer **a**) has been found as the most stable. Another favorable conformation has been shown to bear R flanked by Ph and Me (rotamer **b**). A noteworthy feature was the dearth of the rotamer (R/Ph *anti*) corresponding to **c**. This type of geometry is customarily assumed to be the most stable by organic chemists in stereochemical considerations (bulk repulsive conjecture).

To explore the generality of the above phenomenon and to investigate the principle determining the conformational equi-

A comprehensive literature list for the CH/π interaction is available on the following website: http://www.tim.hi-ho.ne.jp/dioniso

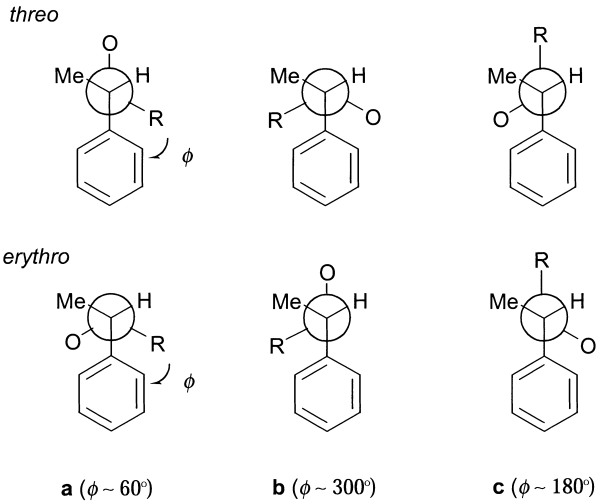


Fig. 2. Three stable conformations of sulfoxide diastereoisomers $CH_3CH(C_6H_5)$–S(O)–R.

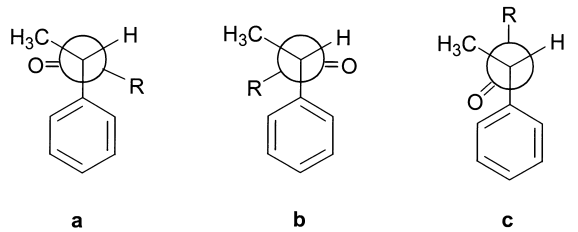


Fig. 3. Three conformations of alkyl 1-phenylethyl ketones, $CH_3CH(C_6H_5)$–CO–R.

librium of organic molecules, here we studied the conformation of a series of alkyl 1-phenylethyl sulfoxides by ab initio MO calculations. We will show that the folded alkyl/phenyl conformation is not "unusual" but prevails generally in these simple aralkyl compounds.

Method

The Gaussian 98 program[10] was used. The basis sets implemented in the program were employed without modification. Electron correlation energies were calculated by applying the second order Møller-Plesset (MP2) perturbation theory. Geometry of the molecules was optimized at the MP2/6-31G(d) level of approximation. Using these geometries, single point calculations were performed at the MP2/6-311G(d,p) level to estimate the conformational energies. Vibrational frequencies were calculated using the analytical second derivatives at the same level of the geometry optimization for each conformer. Using these results, the thermal energy corrections were added to the total energy at 298.15 K and 1 atmosphere of pressure, using the principal isotope for each element type.

Results and Discussion

Table 1 gives relative steric energies of the stable conformations of alkyl 1-phenylethyl sulfoxides $CH_3CH(C_6H_5)$–S(O)–R with differing configurations. Figure 4 gives computer outputs of the methyl analogues (*threo* and *erythro*) as an illustrative example. Table 2 lists interatomic CH/π, CH_3/O, and C^{ortho}–H/O distances at the stable geometry of the respective rotamers.[11]

As expected, rotamer **a** has been calculated to be the most stable, irrespective of the configuration and the nature (bulkiness) of the alkyl group. For ethyl and isopropyl analogues three stable geometries are found, with respect to the rotation around the S–C(alkyl) axis. For these derivatives, a geometry that bears a C^{α}–H bond pointing to the ipso carbon of the phenyl group (thus forming a 5-member CH/π bond) is the most stable. In Fig. 5 are given stereo views for rotamer **a** of the ethyl analogues. Note that the relevant C–H bonds point to the phenyl ring. In rotamer **b**, on the other hand, this type of geometry is not always found to be the most stable (Table 1). This is understandable since, in these cases, a methyl group in ethyl or isopropyl clashes with the benzylic methyl. It may be pointed out in this regard that the torsion angle ϕ corresponding to these geometries (underlined) significantly deviates from the standard value.

Short CH/π distances are noted between an α- or a β-CH in R and the ipso carbon in every case; 2.52–2.73 Å and 2.56–2.72 Å for 5- and 6-member CH/π hydrogen bond, respectively. These values are shorter than the accepted van der Waals

Table 1. Relative Gibbs Free Energies (in kcal mol^{-1}) at 298 K and 1 Atmosphere of Pressure of the Stable Conformations of $CH_3CH(C_6H_5)$–S(O)–R (*threo* and *erythro*), Calculated by the Ab Initio Method, MP2/6-311G(d,p)//MP2/6-31G(d). Optimized Torsion Angles R–S–C–Ph, ϕ/° are Given in the Parentheses. Number in the Bracket for Rotamer **a** and **b** of Ethyl and Isopropyl Analogues Indicates the Number of Atoms Forming the Intramolecular CH/π Hydrogen Bond. See Text for the Underlined Values

(a) *threo*	Rotamer **a**	Rotamer **b**	Rotamer **c**
CH_3	0.00 (66) [5]	1.00 (308) [5]	1.29 (165)
C_2H_5	0.00 (63) [5]	1.46 (307) [5]	1.65 (162)
	0.31 (65) [5]	2.01 (308) [6]	2.27 (169)
	1.67 (62) [6]	3.72 (<u>320</u>) [5]	3.28 (148)
i-C_3H_7	0.00 (62) [5]	1.74 (306) [6]	1.53 (160)
	0.83 (63) [6]	3.19 (<u>322</u>) [5]	3.26 (143)
	2.14 (63) [6]	5.75 (312) [6]	3.49 (147)
t-C_4H_9	0.00 (67) [6]	3.78 (312) [6]	1.16 (144)

(b) *erythro*	Rotamer **a**	Rotamer **b**	Rotamer **c**
CH_3	0.00 (48) [5]	1.03 (298) [5]	3.48 (173)
C_2H_5	0.00 (49) [5]	0.99 (301) [5]	3.15 (176)
	0.57 (46) [5]	2.33 (303) [6]	3.27 (173)
	0.62 (53) [6]	2.70 (<u>295</u>) [5]	5.50 (173)
i-C_3H_7	0.00 (45) [5]	1.54 (302) [6]	3.27 (177)
	0.60 (54) [6]	3.14 (<u>311</u>) [5]	4.73 (172)
	2.35 (55) [6]	5.92 (307) [6]	6.36 (172)
t-C_4H_9	0.00 (56) [6]	3.68 (305) [6]	3.95 (172)

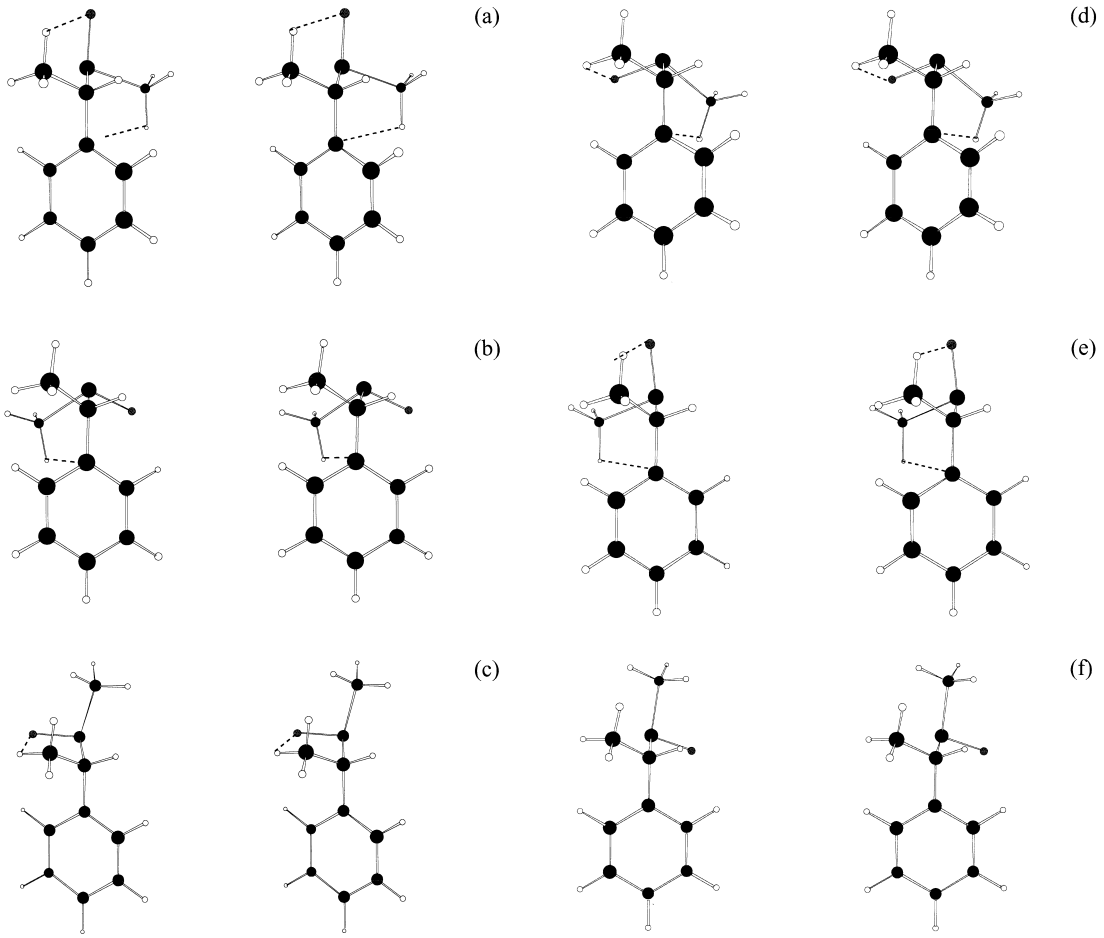


Fig. 4. Stereo views of the methyl sulfoxides as illustrative examples. (a) *threo*-**a**, (b) *threo*-**b**, (c) *threo*-**c**, (d) *erythro*-**a**, (e) *erythro*-**b**, (f) *erythro*-**c**. Note that, in rotamers **a** and **b**, the relevant C–H bond exactly points toward the phenyl ring.

distance (1.2 + 1.7 = 2.9 Å).[12] The results well compare with the data of a crystallographic database survey: 2.63 and 2.70 Å, respectively, for 5- and 6-member intramolecular CH/π bonds.[13]

Another interesting feature of the present results is that rotamer **b** is more stable than rotamer **c** (with two exceptions: R = *i*-C_3H_7 and *t*-C_4H_9, *threo*).[14] In rotamer **b**, R is flanked by Me and Ph. This rotamer has allegedly the most crowded geometry, which organic chemists often neglect in stereochemical considerations. The steric congestion (R vs Me) is certainly severer in rotamer **b** than in rotamer **a**. The difference in Gibbs energy between rotamers **a** and **b** (Δ_{ab}) in fact increases from 1.00 and 1.03 kcal mol^{-1} (R = CH_3) to 3.78 and 3.68 kcal mol^{-1} (*t*-C_4H_9) in the *threo* and *erythro* sulfoxides, respectively.

The CH_3/O interaction between the benzylic methyl group (Me) and the S–O oxygen may stabilize rotamers **a** and **c** in the *threo* sulfoxides, and rotamers **a** and **b** in the *erythro* series. It is noteworthy in this respect that, in rotamer **a**, the R/Ph torsion angle is larger in the *threo* sulfoxides (62–67°) than in the *erythro* series (45–56°). Consequently, the Me/O torsion angle becomes approximately the same (58–67°) in rotamer **a** of both the diastereoisomers. In such geometry, the S–O oxygen and Me come sufficiently close to each other. Distances between one of the three hydrogens of Me and the S–O oxygen atom are in fact found to be short in these geometries (2.55–2.68 Å, 2.36–2.51 Å, and 2.40–2.49 Å, respectively, for rotamer **a** of *threo* sulfoxides, rotamer **b** of *erythro* sulfoxides, and rotamer **c** of *threo*-sulfoxides). The above values are much shorter than the sum of the van der Waals radii of the relevant atoms (1.2 + 1.5 = 2.7 Å); this indicates the importance of this type of hydrogen bond in controlling the conformation of these molecules.

The least favorable geometry is rotamer **c**, which bears R *anti* to Ph. This is understood in terms of the unfavorable electrostatic interaction between the dipole of S–O and the quadrupole of phenyl group.[9] Further, in rotamer **c**, the stabilizing CH/π interaction cannot occur. The differences in Gibbs energy between rotamers **a** and **c** (Δ_{ac}) are smaller in the *threo* series (1.16–1.65 kcal mol^{-1}) than the corresponding values of the *erythro* sulfoxides (3.15–3.95 kcal mol^{-1}). This is reasonable, since two types of CH/O hydrogen bonds (CH_3/O and C^{ortho}–H/O interactions, Fig. 6) may contribute in rotamer **c** of the *threo* sulfoxides. Stabilization from the CH_3/O hydrogen bond cannot be anticipated, on the other hand, in rotamer **c** of the *erythro* sulfoxides. The stabilizing effect of the C^{o}–H/O interaction finds support in the short C–H^{o}/O distances at the respective geometries (Table 2).

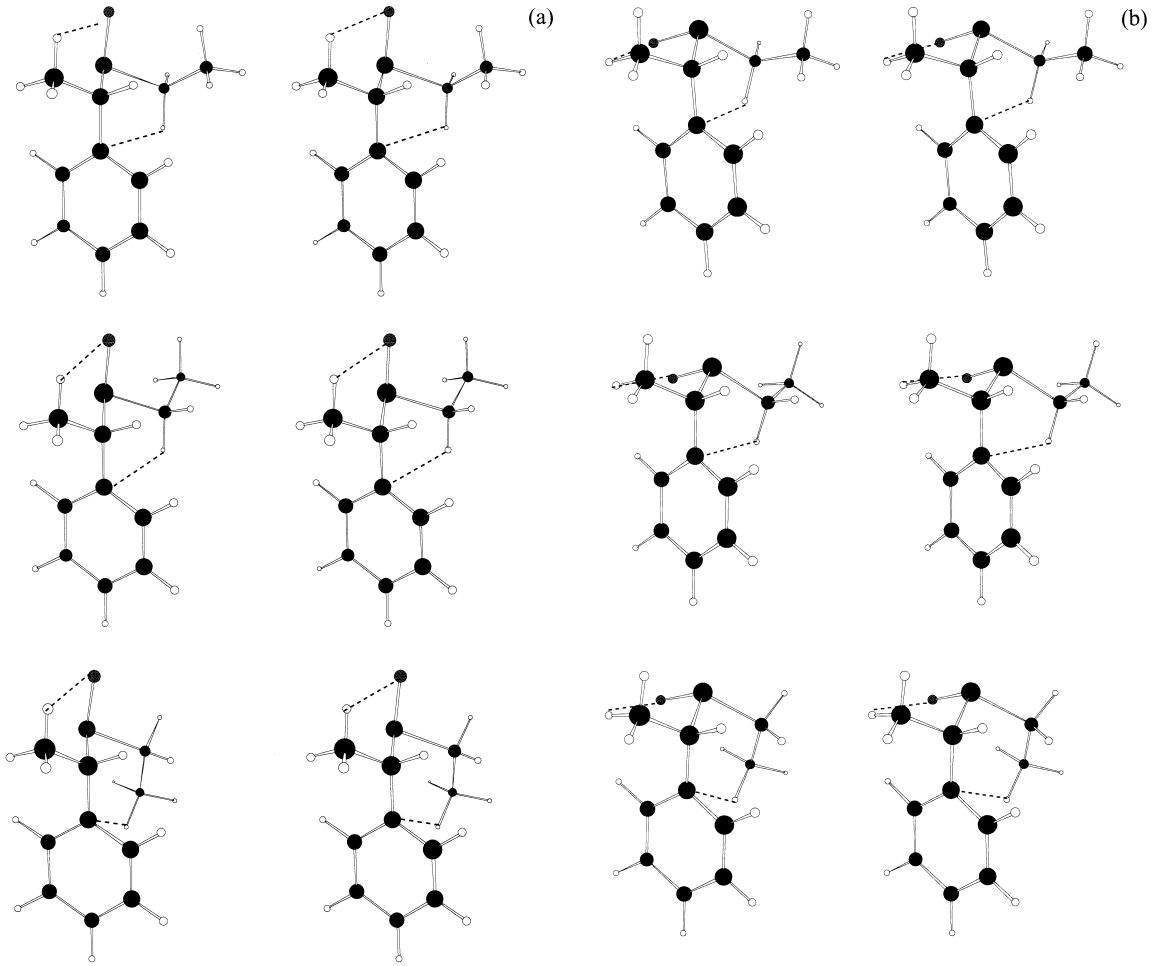


Fig. 5. Stereo views of three stable geometries (each two 5-membered and one 6-membered CH/π-bonded ones) of rotamer **a** of ethyl analogues. (a) *threo*, (b) *erythro*.

Conclusion

The present computational results show that the relative conformational energy is determined by a compromise of various interactions, attractive as well as repulsive. The attractive interactions include the CH/π and CH/O[15] hydrogen bonds. In rotamers **a** and **b**, R is close to Ph and is capable of interacting favorably with the π-system. In rotamers **a** and **c** of *threo* sulfoxides and in rotamers **a** and **b** of *erythro* sulfoxides, CH_3/O hydrogen bond can operate between the benzylic methyl group and the polarized S–O oxygen atom. In rotamers **b** and **c** of *threo* sulfoxides and in rotamers **a** and **c** of *erythro* sulfoxides, the C–H^o/O interaction may operate between an *ortho* CH and the S–O group. The unfavorable interactions are of steric (R vs Me) and electrostatic (O vs Ph) nature.

A similar alkyl/phenyl folded conformation was suggested to prevail for structurally related aralkyl compounds $CH_3CH(C_6H_5)$X–R: ketones (X = CO; NMR)[16] and alcohols (CHOH; IR, NMR).[17] In all of the cases examined, the conformer corresponding to geometries **a** and **b** has been shown to preponderate, irrespective of the nature of the group X (CO, CHOH, SO, or SO_2) and the experimental condition. The above findings are consistent with our recent result obtained by a statistical study of the Cambridge Structural Database;[13] the CH/π-interacted folded structure is often found in crystals as well as in solution. It therefore seems that the alkyl/aryl-congested conformation is not an exception but is the *rule*. It is clear that the dominant force to stabilize the folded conformation is the CH/π interaction.[18] The intramolecular 1,5-CH/O hydrogen bond,[19] where possible, serves for maintaining the stability of these conformations.

The ab initio MO calculations correctly reproduced the experimental data, with regard to the conformational equilibrium of alkyl 1-phenylethyl sulfoxides. Previous force-field calculations[20] predicted rotamer **a** to be the most stable but erroneously suggested rotamer **c** as the next most stable. The failure of the MM2 method in predicting the correct rotameric equilibrium may most probably be due to the negligence of the favorable CH/π and CH/O hydrogen bonds and of the unfavorable O/Ph interaction. We conclude that the necessary parameters for such interactions, underestimated in the past, should be implemented in the future version of force-field programs.

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Table 2. Interatomic C–H/π(ipso), CH_3/O, and C^o–H/O Distances (Å) of the Stable Conformations of Diastereoisomeric Sulfoxides, $CH_3CH(C_6H_5)$–S(O)–R, Calculated by the Ab Initio Method: MP2/6-311G(d,p)//MP2/6-31G(d). Optimized Torsion Angles R–S–C–Ph ϕ/° are Also Given. Number in the Bracket for Rotamer **a** and **b** of the Ethyl and Isopropyl Analogues Indicates the Number of Atoms Forming the Intramolecular CH/π Hydrogen Bond

(a) *threo*					(b) *erythro*				
R	CH/π distance	CH_3/O distance	C^o–H/O distance	ϕ/°	R	CH/π distance	CH_3/O distance	C^o–H/O distance	ϕ/°
CH_3	2.724 [5]	2.642		66 (**a**)	CH_3	2.613 [5]	2.713	2.470	48 (**a**)
	2.629 [5]		2.549	308 (**b**)		2.723 [5]	2.485		298 (**b**)
		2.481	2.543	165 (**c**)				2.779	173 (**c**)
C_2H_5	2.669 [5]	2.662		63 (**a**)	C_2H_5	2.540 [5]	2.724	2.466	49 (**a**)
	2.730 [5]	2.665		65		2.592 [5]	2.667	2.405	46
	2.694 [6]	2.667		62		2.649 [6]	2.755	2.537	53
	2.563 [5]		2.543	307 (**b**)		2.728 [5]	2.471		301 (**b**)
	2.671 [6]		2.584	308		2.721 [6]	2.451		303
	2.562 [5]		2.499	320		2.621 [5]	2.514		295
		2.466	2.577	162 (**c**)				2.773	176 (**c**)
		2.485	2.508	169				2.764	173
		2.425	2.780	148				2.746	173
i-C_3H_7	2.658 [5]	2.683		62 (**a**)	*i*-C_3H_7	2.530 [5]	2.644	2.411	45 (**a**)
	2.672 [6]	2.624		63		2.636 [6]	2.769	2.542	54
	2.630 [6]	2.599		63		2.619 [6]	2.742	2.408	55
	2.668 [6]		2.589	306 (**b**)		2.708 [6]	2.444		302 (**b**)
	2.519 [5]		2.503	322		2.586 [5]	2.428		311
	2.638 [6]		2.511	312		2.637 [6]	2.383		307
		2.438	2.590	160 (**c**)				2.766	177 (**c**)
		2.462	2.898	143				2.757	172
		2.402	2.788	147				2.802	172
t-C_4H_9	2.561 [6]	2.552		67 (**a**)	*t*-C_4H_9	2.564 [6]	2.740	2.409	56 (**a**)
	2.581 [6]		2.510	312 (**b**)		2.568 [6]	2.358		305 (**b**)
		2.416	2.857	144 (**c**)				2.818	172 (**c**)

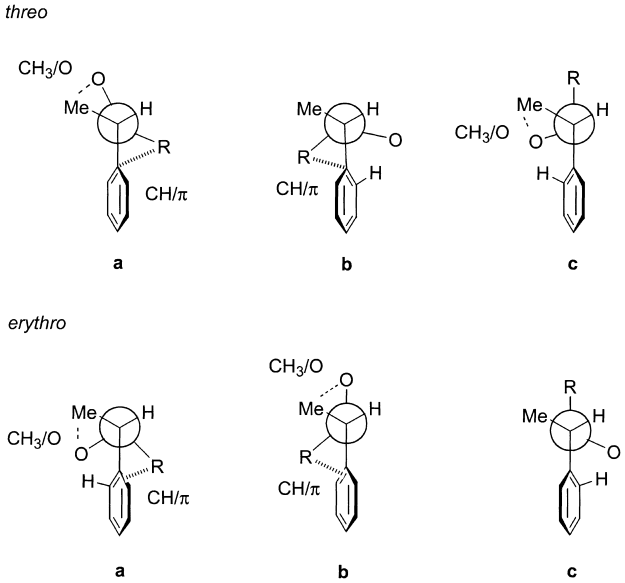

Fig. 6. CH/π and CH/O interactions suggested for *threo* and *erythro* sulfoxides.

thors thank the Information Media Center at Hiroshima University for the use of H9000 VR360 and the Research Center for Computational Science, Okazaki National Research Institutes for the use of the Fujitsu VPP5000.

References

1 Y. Iitaka, Y. Kodama, K. Nishihata, and M. Nishio, *J. Chem. Soc., Chem. Commun.*, **1974**, 389.

2 Y. Kodama, K. Nishihata, M. Nishio, and Y. Iitaka, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 1490.

3 M. Hirota, Y. Takahashi, M. Nishio, and K. Nishihata, *Bull. Chem. Soc. Jpn.*, **51**, 2358 (1978).

4 Y. Kodama, S. Zushi, K. Nishihata, M. Nishio, and J. Uzawa, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 1306.

5 Here we employ the conventional *threo-erythro* notation to avoid confusion. The sequence-rule symbol does not necessary match the stereochemical structure. Thus, e.g., (α*R*,S*S*/α*S*,S*R*)-*t*-butyl-1-phenylethyl sulfoxide corresponds, configurationally, to (α*R*,S*R*/α*S*,S*S*)-alkyl-1-phenylethyl sulfoxide (alkyl = CH_3, C_2H_5, *i*-C_3H_7).

6 Y. Kodama, K. Nishihata, M. Nishio, and N. Nakagawa, *Tetrahedron Lett.*, **24**, 2105 (1977).

7 M. Nishio, M. Hirota, and Y. Umezawa, "The CH/π Interaction. Evidence, Nature, and Consequences," Wiley-VCH, New York (1998).

8 Recent examples: M. Matsugi, M. Nojima, Y. Hagimoto,

and Y. Kita, *Tetrahedron Lett.*, **42**, 6903 (2001); M. Matsugi, M. Nojima, Y. Hagimoto, and Y. Kita, *Tetrahedron Lett.*, **42**, 8019 (2001); M. Kitamura, K. Nakano, T. Miki, M. Okada, and R. Noyori, *J. Am. Chem. Soc.*, **123**, 8939 (2001); Y. Miyake, A. Hosoda, M. Tamagaki, E. Nomura, and H. Taniguchi, *Chem. Commun.*, **2002**, 132; Y. Kitahara and K. Tanaka, *Chem. Commun.*, **2002**, 932; Y. Yoshitake, J. Misaka, K. Setoguchi, M. Abe, T. Kawaji, M. Eto, and K. Harano, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1611.

9 O. Takahashi, K. Yasunaga, Y. Gondoh, Y. Kohno, K. Saito, and M. Nishio, *Bull. Chem. Soc. Jpn.*, **75**, 1777 (2002).

10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, "Gaussian 98, Revision A.4," Gaussian, Inc., Pittsburgh PA (1998).

11 It is noted that CH/π distances calculated with the use of MP2/6-31G(d) optimized geometry are shorter than those obtained by the HF/6-31G(d) level optimization (data not shown). This is reasonable on the ground of general understanding that, for the CH/π interaction, a large part of the stabilization comes from the correlation energy (see Ref. 9). The conformational energy and the CH/π distance calculated with MP2/6-31G(d,p) optimized geometry are not significantly different from those obtained by MP2/6-31G(d) level of optimization.

12 L. Pauling, "The Nature of the Chemical Bonds," Cornell Univ. Press, Ithaca, New York (1960), p. 260.

13 Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa, and M. Nishio, *Tetrahedron*, **55**, 10047 (1999).

14 This is in conflict with our earlier suggestion by NMR that rotamer **c** is preferred to rotamer **b** in the conformational equilibrium of the *t*-butyl analogues. The reason remains unclear but it is probable that the experiments [simulation of the lanthanoid shift reagent (LSR) induced NMR chemical shifts] gave an erroneous conclusion due to inappropriate model in the simulation procedure (e.g., wrong assumption for the LSR···O–S distance or the lanthanide distribution).

15 G. R. Desiraju and T. Steiner, "The Weak Hydrogen Bond in Structural Chemistry and Biology," Oxford Univ. Press, Oxford (1999).

16 S. Zushi, Y. Kodama, K. Nishihata, K. Umemura, M. Nishio, J. Uzawa, and M. Hirota, *Bull. Chem. Soc. Jpn.*, **53**, 3631 (1980).

17 J. Uzawa, S. Zushi, Y. Kodama, Y. Fukuda, K. Nishihata, K. Umemura, M. Nishio, and M. Hirota, *Bull. Chem. Soc. Jpn.*, **53**, 3623 (1980).

18 Importance of the CH/π interaction and its hydrogen bond nature has been shown by recent high-level ab initio calculations: See: J. J. Novoa and F. Mota, *Chem. Phys. Lett.*, **318**, 345 (2000); S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Am. Chem. Soc.*, **122**, 3746 (2000); M. Oki, S. Takano, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **73**, 2221 (2000); S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, and K. Tanabe, *J. Phys. Chem. A*, **106**, 4423 (2002).

19 H. Yoshida, I. Kaneko, H. Matsuura, Y. Ogawa, and M. Tasumi, *Chem. Phys. Lett.*, **196**, 601 (1992); H. Yoshida, T. Tanaka, and H. Matsuura, *Chem. Lett.*, **1996**, 637; H. Yoshida, T. Harada, K. Ohno, and H. Matsuura, *Chem. Commun.*, **1997**, 2213; S. Tsuzuki, H. Houjou, Y. Nagawa, and K. Hiratani, *J. Chem. Soc., Perkin Trans. 2*, **2001**, 1951.

20 M. Hirota, T. Sekiya, K. Abe, H. Tashiro, M. Karatsu, M. Nishio, and E. Osawa, *Tetrahedron*, **39**, 3091 (1983).