Use of Achiral Shift Reagents to Indicate Relative Stabilities of Diastereomeric Solvates

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In the presence of chiral aryl perfluoroalkylcarbinols, the NMR spectra of sulfoxide enantiomers are nonequivalent. Addition of an achiral lanthanide shift reagent, $Eu(fod)_3$, alters the magnitude and sometimes the sense of this nonequivalence. Mechanisms underlying this "alteration" are discussed and the shape of the nonequivalence vs. $Eu(fod)_3$ curves is related to nonidentical energies of solvation of the sulfoxide enantiomers by the chiral carbinol. These energy differences are in turn related to the structure and stereochemistry of the sulfoxides via specific carbinol–sulfoxide solvation models. The application of chiral solvent–achiral shift reagent systems to the determination of the absolute configurations of enantiomeric solutes is considered.

A continuing interest in the mechanisms by which chiral molecules distinguish between enantiomers has prompted us to explore new methods of obtaining information regarding the strengths of diastereomeric interactions between chiral molecules. Such information is essential to rational design of asymmetric induction reactions and to the direct chromatographic resolution of enantiomers. We now describe a method employing chiral solvents and achiral shift reagents which not only provides this information but also affords results relevant to the question of whether chiral solvent–achiral shift reagent systems can be used to determine absolute configurations in a manner analogous to that used for chiral solvents alone.[1-4]

Mixed chiral solvent–achiral shift reagent systems have been reported[5] by Jennison and Mackay to enhance NMR spectral nonequivalence for enantiomeric solute molecules beyond that observed in the chiral solvent alone. The mechanism underlying this enhancement was not delineated, however. Similarly, Whitesides et al have reported[6] that the addition of $Eu(fod)_3$ to a solution of resolved *N*-methyl-1-phenylethylamine containing partially resolved 1-phenylethylamine produces enantiomeric nonequivalence in the ^1H NMR spectra of the latter. These authors present data to support the contention that this nonequivalence stems from formation of spectrally dissimilar rapidly exchanging diastereomeric 1:1:1 complexes of $Eu(fod)_3$, chiral *N*-methyl-1-phenylethylamine and 1-phenylethylamine. Considered and excluded as the source of the nonequivalence was an alternate mechanism in which $Eu(fod)_3$ preferentially complexes whichever of the 1-phenylethylamine enantiomers that most weakly interacts with the chiral *N*-methyl-1-phenylethylamine. Even more recently, Ajisaka and Kainosho have reported that partially resolved α-phenylethylamine shows enantiomeric ^1H NMR nonequivalence upon addition of $Eu(fod)_3$.[7] These workers suggest that such nonequivalence originates from the formation of transient diastereomeric 2:1 amine–$Eu(fod)_3$ complexes having nonidentical chemical shifts. This mechanism is very similar to that espoused by Whitesides.[6] Ajisaka and Kainosho also rule out[8] the alternate mechanism earlier considered and excluded by Whitesides.[6]

Although apparently unimportant among the systems studied by Whitesides et al.[6] or by Ajisaka and Kainosho,[7] this latter type of mechanism is fundamentally reasonable and seems more likely to be observed for strong diastereomeric interactions than for weak ones. Prior studies of the interactions of chiral solvents with enantiomeric solutes suggest several such systems, and evidence is herein presented that dissimilar stabilities of diastereomeric solvates can be demonstrated through the agency of achiral lanthanide shift reagents.

Using the terms R and S to designate the solute enantiomers, C to represent the chiral solvent, and L to represent the achiral lanthanide shift reagent, eq 1–7 represent reactions which play a role in determining the time-averaged chemical shifts of the solute enantiomers. Other reactions

$$R + C \overset{K_1}{\rightleftharpoons} RC \quad (1)$$

$$S + C \overset{K_2}{\rightleftharpoons} SC \quad (2)$$

$$R + L \overset{K_3}{\rightleftharpoons} RL \quad (3)$$

$$S + L \overset{K_3}{\rightleftharpoons} SL \quad (4)$$

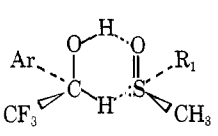
$$RC + L \overset{K_4}{\rightleftharpoons} RCL \quad (5)$$

$$SC + L \overset{K_5}{\rightleftharpoons} SCL \quad (6)$$

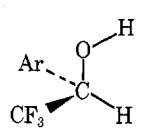
$$C + L \overset{K_6}{\rightleftharpoons} CL \quad (7)$$

occur and can be described (e.g., $2L \rightleftharpoons L_2$; $2R + L \rightleftharpoons R_2L$; $2S + L \rightleftharpoons S_2L$; $R + S + L \rightleftharpoons RSL$; $2C \rightleftharpoons C_2$; $2S \rightleftharpoons S_2$; $2R \rightleftharpoons R_2$; $R + S \rightleftharpoons RS$) but will be considered as unimportant to the bulk of the subsequent discussion, even though some of them are essential to the Ajisaka–Kainosho mechanism.[7]

Chiral type 1 alcohols have been proposed[1] to interact with sulfoxide enantiomers to afford two rapidly exchanging diastereomeric 1:1 solvates which spend a significant fraction of time in the chelate-like conformations **2a** and **2b**. Although these diastereomeric solvates may have noni-



2a



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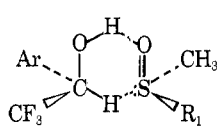


2b

dentical formation constants, K_1 and K_2, the strength of these principle interactions ensures that essentially all of both sulfoxide enantiomers will be hydrogen bonded *if a severalfold excess of the alcohol is used.* Under these conditions, spectral differences between enantiomers arise not from differential degrees of solvation but rather from intrinsic spectral nonidentity of the conformers, **2a** and **2b.** In the stereochemical situation depicted, the resonance of the sulfinyl methyl will, owing to shielding by the cis aryl group, occur at higher field for the enantiomer incorporated into **2b** than for the one in **2a.** The converse holds for the substituent R_1. During the subsequent discussion, nonequivalence arising via this mechanism will be termed "type A" nonequivalence.

Type 1 alcohols are fairly acidic and, while they solvate the basic sulfoxides strongly, they interact only weakly

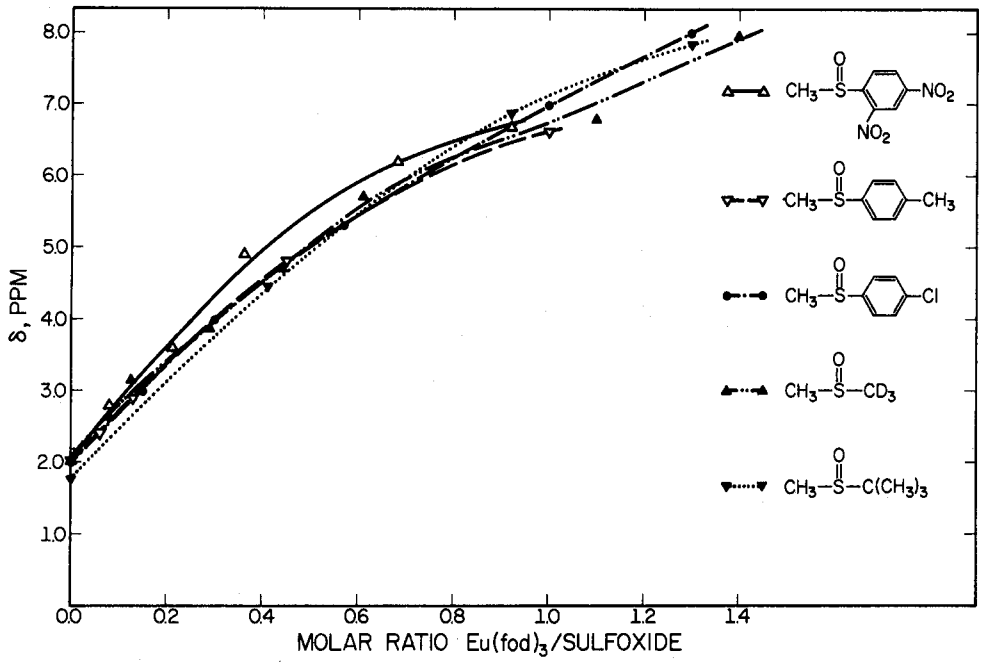


Figure 1. The influence of $Eu(fod)_3$ concentration upon the chemical shifts of the sulfinyl methyls of several methyl sulfoxides. Samples are ca. 0.2 *M* in sulfoxide and 0.6 *M* in chiral carbinols **4** or **5**.

with $Eu(fod)_3$ (i.e., K_6 is small) as evidenced by the small chemical shifts induced by addition of the latter. $Eu(fod)_3$ is a strong Lewis acid and, again judging by induced shifts, interacts more strongly with sulfoxides than do type 1 alcohols (i.e., $K_3 > K_1$ or K_2).[9] If the $Eu(fod)_3$ preferentially strips enantiomeric sulfoxide from the least stable of the diastereomeric alcohol–sulfoxide solvates, then that sulfoxide enantiomer will tend to have its time averaged chemical shifts at lower field than those of the enantiomer incorporated into the more stable solvate (type B nonequivalence). This will be true *regardless of the initial relative chemical shift positions of the enantiomers observed in the chiral solvent alone.* By relating type B nonequivalence to the nonidentical formation constants (K_1 and K_2) of the two diastereomeric alcohol–sulfoxide solvates, one predicts that, in situations where no difference in stability exists (K_1 equals K_2), the addition of the lanthanide reagent will simply attenuate the type A nonequivalence initially induced by the chiral alcohol. This situation will obtain for many meso compounds and for compounds enantiomeric by virtue of isotopic substitution.[10] Further, addition of sufficient shift reagent to strip all sulfoxide from the chiral alcohol should cause type B nonequivalence to vanish. These predictions differ from the results expected via the mechanism operative in the work reported by Whitesides.[6] For example, if nonequivalence stemmed solely from formation of spectrally nonidentical diastereomeric 1:1:1 complexes of shift reagent, sulfoxide, and chiral solvent (type C nonequivalence), one would not expect excess (relative to sulfoxide) $Eu(fod)_3$ to cause nonequivalence to vanish and one would expect to see nonequivalence for meso and isotopically chiral molecules. Moreover, the possibility that these 1:1:1 diastereomeric complexes may be formed to different extents provides additional mechanisms for nonequivalence even if the 1:1:1 diastereomers have identical spectra. If addition of the chiral alcohol to a 1:1 sulfoxide–$Eu(fod)_3$ complex increases the coordination number of the europium ion, spectral changes can be expected to occur for bound ligands. In general, limiting shifts for 2:1 solute–lanthanide complexes are not as great as those of the 1:1 complexes.[11] Hence, differential extents of formation of diastereomeric 1:1:1 complexes may cause nonequivalence of the sulfoxide enantiomers. These concentration differences can result either from nonidentical formation constants ($K_4 \neq K_5$; type D nonequivalence) or, even if K_4 equals K_5, nonidentical K_1 and K_2 values will result in nonidentical concentrations of the 1:1:1 complexes. In this event, the nonequivalence thus induced (type E) will be opposite in sense to that of the type B mechanism. Realistically, one should expect simultaneous contributions from all nonequivalence mechanisms. However, for a given system, the relative contribution of each mechanism will be concentration and temperature dependent.

Consider a sample containing (*R*)-enriched methyl sulfoxide, CCl_4, and a threefold excess of (*R*)-2,2,2-trifluoro-1-(10-bromo-9-anthryl)ethanol (**3**).[12] Under these type A conditions, the sulfinyl methyl resonance of the *S* enantiomer occurs at higher field than that of the *R* enantiomer. Subsequent progressive addition of $Eu(fod)_3$ shifts all the sulfoxide resonances downfield, the sulfinyl methyl resonances being most strongly shifted (Figure 1). The initial increments of $Eu(fod)_3$ can either strip sulfoxide from the chiral alcohol ($K_3 > K_1$ or K_2, $K_3 > K_4$ or K_5) or add to the 1:1 solvates to form 1:1:1 complexes ($K_3 < K_4$ or K_5). If the first situation prevails, then, for a sulfoxide where K_1 equals K_2 and K_4 equals K_5, an experimental plot of observed nonequivalence vs. the concentration of $Eu(fod)_3$ should be approximately a straight line which reaches zero and remains there when the $Eu(fod)_3$ concentration equals or exceeds that of the sulfoxide. This is essentially the case with methyl trideuteromethyl sulfoxide (Figure 2). Note that the nonequivalence initially shown by the enantiomers of this sulfoxide is attenuated by the addition of $Eu(fod)_3$ and reaches zero after the lanthanide:sulfoxide ratio exceeds 1:1. This is in accord with the proposed requirement that the diastereomeric solvates be of different stability in order that nonequivalence of types B, D, or E be observable. Here, such stability difference would be isotopic in origin and quite small. This result also suggests that type C nonequivalence makes little contribution in this instance. If 2:1 (rather than 1:1) complexes of Me_2SO–$Eu(fod)_3$ were being formed to an appreciable extent, the nonequivalence should, within the framework of the assumptions involved in this model, be observed to diminish to zero at $Eu(fod)_3$–

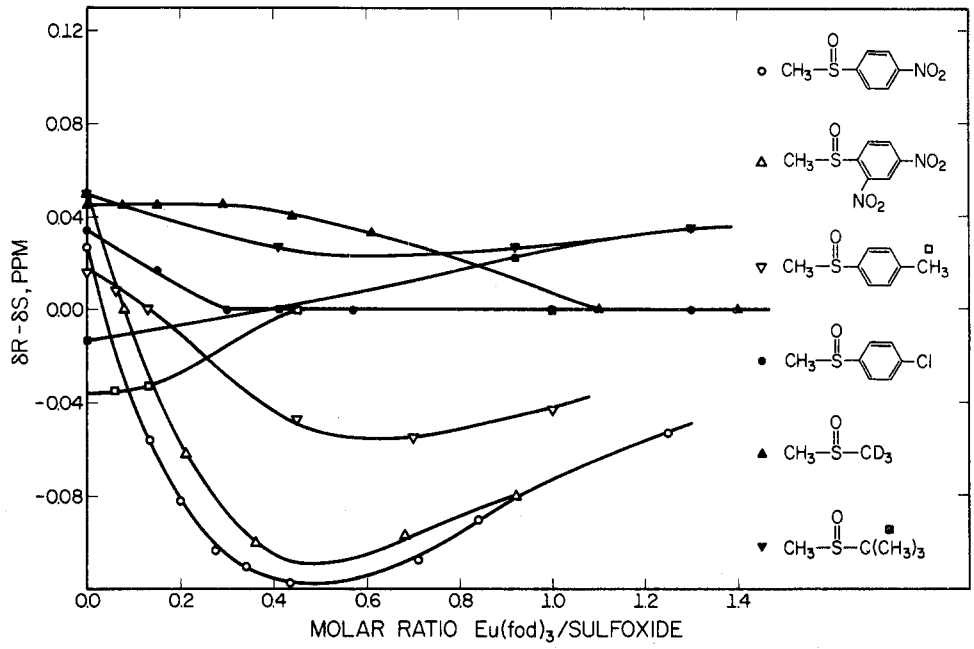


Figure 2. The influence of $Eu(fod)_3$ concentration upon the magnitudes and senses of nonequivalence of several methyl sulfoxides (0.2 *M*) in the presence of *R* carbinols **4** or **5** (0.6 *M*).

Me_2SO ratios of less than unity. While formation of diastereomeric 2:1 sulfoxide–$Eu(fod)_3$ complexes could, in principle, afford nonequivalence for partially resolved sulfoxides via the Ajisaka–Kainosho mechanism,[7] such nonequivalence would, in the case of methyl trideuteriomethyl sulfoxide, be isotopic in origin. No such nonequivalence is noted in the absence of chiral alcohol **3**.

In the case of methyl *tert*-butyl sulfoxide, solvate **2b** (R_1 = *tert*-butyl) is expected on steric grounds to be more stable than solvate **2a** in which the bulky anthryl and *tert*-butyl groups are cis. If this situation obtains, the type B model predicts that the sign of the *tert*-butyl (but not the sulfinyl methyl) nonequivalence will invert and that the magnitudes of both nonequivalences will approach zero with increasing lanthanide concentration. Initially, these predictions are borne out. However, high lanthanide:sulfoxide ratios do not cause nonequivalence magnitudes to become zero, presumably as a consequence of the occurrence of significant type D (and perhaps type C) nonequivalence in this concentration range. Nonequivalence of the Ajisaka–Kainosho type would also disappear at high lanthanide:sulfoxide ratios.[7] The extent to which the type E mechanism occurs and counteracts the type B mechanism will depend upon the magnitudes of several equilibrium constants (K_1–K_5). A priori, it seems unlikely that the type E mechanism can dominate the type B mechanism, since type **1** carbinols coordinate but weakly to $Eu(fod)_3$. Moreover, the ratio of the E/B contributions is smaller at low $Eu(fod)_3$/sulfoxide ratios owing to the effect of mass action.

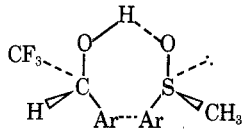
In the case of methyl *p*-tolyl sulfoxide, the a priori prediction of the stability order (**2a** vs. **2b**) of the diastereomeric solvates is complicated by considerations of steric vs. electronic interactions. Solvate **2b**, in which the 10-bromo anthryl substituent of the alcohol is cis to the *p*-tolyl group, will be the most stable provided that the electronic effects of π–π bonding and trifluoromethyl–*p*-tolyl repulsion[13] dominate possible steric repulsion between the two aryl groups. This is apparently the case since addition of $Eu(fod)_3$ causes inversion in the sign of the sulfinyl methyl nonequivalence. Addition of 0.5 molar equiv of $Eu(fod)_3$ to a 30% enriched sample of this sulfoxide in carbon tetrachloride affords no Ajisaka–Kainosho-type nonequivalence. Similarly, no nonequivalence is afforded upon subsequent addition of racemic carbinol **4**. Clearly, the presence of the chiral carbinol is essential for the observation of nonequivalence in these systems.

Methyl *p*-chlorophenyl sulfoxide behaves approximately as does methyl *p*-tolyl sulfoxide but does not actually show inversion of the sense of nonequivalence of the sulfinyl methyl, presumably as a consequence of the increasing importance of offsetting type C, D, and/or E contributions as the $Eu(fod)_3$ concentration is increased. However, the rate of increase of the observed nonequivalence is initially too rapid to be simply attenuation of the type A contribution.

To amplify energy differences between diastereomeric solvates, a system comprised of slightly enriched (*S*)-(−)-methyl 2,4-dinitrophenyl sulfoxide (**4**) and (*R*)-2,2,2-trifluoro(10-methyl-9-anthryl)ethanol (**5**)[12] was chosen. In this case, the assignment of absolute configuration to the sulfoxide. Since type B nonequivalence stems from the nonidentity of K_1 and K_2, the increased amplitude of the signment leads to a curve of the same general shape as that observed for the configurationally known methyl *p*-tolyl sulfoxide. Since type B nonequivalence stems from the nonidentity of K_1 and K_2, the increased amplitude of the curve bespeaks a larger energy difference between these diastereomeric solvates. Mixtures of this sulfoxide and alcohol **5** are red, consistent with the formation of π–π complexes, as is the inverse temperature dependence of the intensity of this red color. Note also that the change of slope which occurs at a lanthanide:sulfoxide ratio of ca. 0.5 is especially indicative of the type B mechanism, since it is at just this value that maximum type B nonequivalence should occur for a *racemic solute*.[14]

Finally, it should be noted that crystallization of racemic methyl 2,4-dinitrophenyl sulfoxide from a carbon tetrachloride solution of (*R*)-2,2,2-trifluoro(10-methyl-9-anthryl)ethanol affords mother liquors enriched in the enantiomer showing low-field type A nonequivalence. The crystalline material is oppositely enriched. This enrichment is consistent with the existence of energetically dissimilar diastereomeric solvates; the enantiomer preferentially retained (complexed) in the mother liquors *is the one predicted by the solvation model.* Since similar results ob-

tained either on crystallization of racemic 4 from or dissolution in solutions containing (*R*)-2,2,2-trifluoro(9-anthryl)ethanol,[12] it appears that the enrichment is thermodynamic rather than kinetic in origin. Although the extent of enantiomeric enrichment of the mother liquors is appreciable (ca. 10%), it is not so great as to suggest that only one enantiomer of 4 can simultaneously hydrogen bond and π complex to the carbinol. Because of the presumed greater strength of the π complex (in this instance) than the carbinyl hydrogen bonding interaction, it is deemed likely that solvation energy differences reflect the presence of the carbinyl hydrogen bonding interaction in one diastereomer but not the other. In this event, conformer **2a** remains the important conformer for the *R* sulfoxide but conformer **6** may now be the important conformer for the solvate derived from *R* alcohol and *S* sulfoxide. Supportive of this



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point is the observation that racemic methyl *p*-nitrophenyl sulfoxide and carbinol **5** afford a curve very similar to that of dinitrophenyl sulfoxide **4**,[15] if one accepts the configurational assignments based upon the sense of the type A nonequivalence. In the case of (−)-methyl 2,4-dinitrophenyl sulfoxide, the *S* configuration follows from the sense of the type A nonequivalence and from the similarity of curve shape (Figure 2) obtained using this assignment to those of the configurationally known methyl *p*-tolyl and methyl *p*-chlorophenyl sulfoxides.

In principle, the six equilibrium constants (eq 1–7) can be obtained for a sulfoxide via an iterative computational process which matches calculated and experimental curves. Additional curves obtained at other concentration levels would facilitate this matching. Even without computation, however, one can roughly equate the depth of the minimum shown by the curves in Figure 2 with the stability differences between the diastereomeric solvates. Such comparison requires that all the curves be obtained under similar conditions and that one *assume* that the R_1 substituent has a negligible effect upon the chemical shifts of the sulfinyl methyls in the sulfoxide containing species present. The similarity of the curves in Figure 1 show this not to be an unreasonable approximation.

In view of the several nonequivalence mechanisms potentially operable, it is clear that *generalized* correlations between the senses of nonequivalence observed in chiral solvent–achiral shift reagent systems and the absolute configurations of the solutes are unwarranted. However, in systems where solvent–solute interactions are understood, the spectral perturbations attending the addition of achiral shift reagents can provide supportive data for assignment of absolute configurations.

It is manifest from the preceding discussions that addition of an achiral shift reagent to a partially resolved solute is potentially capable of producing enantiomeric spectral nonequivalence by a mechanism other than that of Ajisaka and Kainosho.[7] Indeed, both types of nonequivalence, arising as it were from the partially resolved solute serving as a chiral solvent, could also occur for *chiral* lanthanide shift reagents and thus either counteract or reinforce any nonequivalence stemming from the chirality of the shift reagent. Such contributions further complicate the assignment of absolute configuration through the use of chiral lanthanide shift reagents.[16–19]

One obvious application for NMR experiments of this kind is the screening of compounds potentially useful as chiral stationary phases for the direct chromatographic resolution of enantiomers. The chiral compound being screened need not be capable of inducing type A nonequivalence for this approach to succeed.

Experimental Section

General NMR Procedure. Samples of the sulfoxide and the chiral alcohol were weighed into an NMR tube and dissolved in 0.5 ml of CCl_4. The spectrum of this solution was determined before and after successive additions of solid $Eu(fod)_3$. Relative concentrations were determined through comparison of the integrals of the *tert*-butyl ligand resonance and the sulfinyl methyl resonances.

$Eu(fod)_3$ was used as obtained from Aldrich Chemical Co. and the CCl_4 (J. T. Baker reagent grade) was used without further purification. All spectra were taken on a Varian A-60A spectrometer at 44°C.

Sulfoxides. Partially resolved samples of the *tert*-butyl, trideuteriomethyl, *p*-tolyl, and *p*-chlorophenyl methyl sulfoxides were prepared by the method of Andersen and have been previously reported.[20,21,22] Partially resolved nitro-substituted aryl methyl sulfoxides are not readily obtained by Andersen's approach owing to reaction of nitro groups with Grignard reagents. However, racemic *p*-nitrophenyl[23] and 2,4-dinitrophenyl methyl[24] sulfoxides have been reported.

Partial Resolution of 2,4-Dinitrophenyl Methyl Sulfoxide. The solution obtained by stirring 30 mg of racemic sulfoxide and 25 mg of (*S*)-(+) − **5** in 1 ml of carbon tetrachloride for 4 hr at 25° was filtered to remove undissolved sulfoxide and found to be enriched (ca. 10% e.e.) in the sulfoxide enantiomer showing a low field sense of sulfinyl methyl nonequivalence. Similar results are obtained by allowing the sulfoxide to crystallize from an initially hot solution of similar composition. A partially resolved *S*-enriched sample of the sulfoxide of 17% enantiomeric purity, obtained in an alternate manner, shows $[\alpha]^{25}D$ −15.4° (*c* 0.49, dichloromethane).

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Registry No.—Methyl 2,4-dinitrophenyl sulfoxide, 56454-35-4; methyl *p*-tolyl sulfoxide, 39066-80-3; methyl *p*-chlorophenyl sulfoxide, 56487-58-2; methyl trideuteriomethyl sulfoxide, 56487-59-3; methyl *tert*-butyl sulfoxide, 49775-44-2; methyl *p*-nitrophenyl sulfoxide, 56454-34-3.

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(8) Although it is probably correct to consider this alternate mechanism as relatively unimportant *in this case*, the grounds for excluding it seem less than rigorous. The experimental demonstration that racemic and enantiomerically pure α-phenylethylamine are isochronous does not necessarily demonstrate the absence of strong diastereomeric solute–solute interactions.
(9) Infrared measurements show that the association constant between Me_2SO and 2,2,2-trifluoro-1-phenylethanol is ca. 200 in carbon tetrachloride whereas the association constant for 1:1 interaction between Me_2SO and $Eu(fod)_3$ in CCl_4 has been reported to be 625. See J. Reuben, *J. Am. Chem. Soc.*, **95**, 3534 (1973).
(10) For meso compounds containing but one group complexable by $Eu(fod)_3$ or the chiral solvent (e.g., 2-propanol), type B nonequivalence cannot be observed in principle. However, for meso compounds of the type $R(CH_2)_nS$, where R and S are enantiotopic and contain complexable groups, nonequivalence originating from the formation of 1:1:1 complexes can result but is of type C or D. Jennison and Mackay report[5] several instances where meso compounds fail to show perceptible nonequivalence in chiral solvent–achiral shift reagent systems.
(11) It has been noted [D. F. Evans and M. Wyatt, *J. Chem. Soc., Dalton Trans.*, 765 (1974)] that the limiting shifts of 2:1 solute–lanthanide complexes are smaller than those of the 1:1 complexes. In particular, the limiting shift of the 2:1 Me_2SO–$Eu(fod)_3$ complex is 3.48 ppm whereas that of the 1:1 adduct is 6.58 ppm. It should be clear that the 2:1 complexes discussed are restricted to those where the lanthanide ion is di-

rectly coordinated to the solutes. A referee has correctly observed that limiting shifts depend upon the geometry of the complexes and that the generalization, while possibly true for sulfoxides, is not necessarily true for all other substrates.
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(14) The position of the minimum should reflect the enantiomeric purity of the solute provided types C and D nonequivalence make negligible contributions.
(15) The Ajisaka–Kainosho mechanism[7] cannot be operative for racemic solutes. Hence, the observation of nonequivalence for racemic **4**, racemic methyl *p*-nitrophenyl sulfoxide, and unlabeled Me_2SO must have a different origin.
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Carbon-13 Nuclear Magnetic Resonance Studies of Organoboranes The Relative Importance of Mesomeric B–C π-Bonding Forms in Alkenyl- and Alkynylboranes[1]

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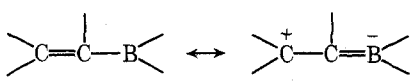
The ^{13}C NMR spectra have been obtained for trialkylboranes, dialkylborinates, alkylboronates, dialkylchloroboranes, alkenylboranes, and alkynylboron derivatives. In the alkenyl- and alkynylboranes, it is concluded on the basis of the ^{13}C NMR chemical shifts that π interaction between the π-electron system and the vacant p orbital of the boron atom exists to a certain extent, and that the mesomeric B–C π-bonding forms contribute to the ground state of these α,β-unsaturated compounds.

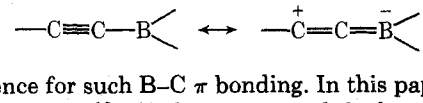
The question of B–C π bonding in alkenylboranes has presented chemists with an intriguing problem (eq 1).[3]



(1)

Though a substantial body of evidence now exists supporting π interaction between the π-electron system and the vacant p orbital of boron in an alkenylborane,[3] objection against such π bonding has also been raised.[3a] The large volume of experimental data gathered so far has been obtained by infrared,[4-10] Raman,[10] ultraviolet,[7,8,11] ^1H NMR,[8] ^{11}B NMR,[7,8] ^{19}F NMR,[7,12,13] and photoelectron[14] spectroscopic techniques, data which seem to provide mainly indirect evidence. The question has also been the subject of LCAO–MO–SCF,[11] CNDO,[15,16] and INDO[17] calculations. However, ^{13}C NMR spectra have not as yet been obtained, despite the superior advantage that their chemical shifts can more directly provide insight into the bonding situations.[18,19]

Alkynylboranes may also exist in the mesomeric allenyl form (eq 2),[3a] though to our knowledge there is no literature evidence for such B–C π bonding. In this paper, we report in full on the ^{13}C NMR spectra and the bonding situation of alkenyl- and alkynylboranes.



(2)

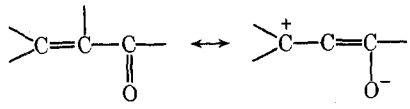
Experimental Section

All boranes were prepared as previously described.[20] ^{13}C NMR spectra were measured on a Varian XL-100-15 spectrometer operating in the Fourier transform mode at 25.2 MHz. All spectra were determined with noise-modulated proton decoupling. Single-frequency off-resonance decoupled spectra were used to assign the resonances in questionable cases. The spectra were taken in benzene-d_6 (ca. 50% concentration), except where otherwise indicated, in 12-mm sample tubes, and were calibrated using the solvent resonances as secondary standards.

Results and Discussion

The chemical shifts obtained from the ^{13}C NMR spectra of alkenyl- (**1–5**), alkynyl- (**6** and **7**), and alkylboron derivatives (**8–14**), and those of the corresponding alkenes, alkynes, and alkanes are listed in Tables I–III. Assignments of ^{13}C signals were made on the basis of (1) off-resonance decoupling spectra, (2) consistency with other shift data,[18,19] and (3) broadening and weakening of the peak corresponding to the ^{13}C nuclei directly attached to boron. The last phenomenon was generally observed for the alkyl- and alkenylboranes, and is presumably due to large carbon–boron couplings which are incompletely relaxed by the quadrupole mechanism.[21,22] In the case of the alkynylboranes, the absorption of the α carbon had completely disappeared.

As is apparent from Table I, the chemical shifts at C_1 and C_2 of **1** are similar to those of acrylic acid (δ C_1 128.0, δ C_2 131.9).[18] Also, the shifts in the other alkenylboranes show an analogous trend to those in α,β-unsaturated carbonyl compounds, where the contribution of enolate form is important (eq 3).[18,19]



(3)

This phenomenon is highly interesting in connection with the relationship between the ^{13}C shielding and the chemical reactivity of boron derivatives, since the suggestion that many reactions of aldehydes and ketones have counterparts in the reactions of trialkylboranes has already been presented.[23]

The $^{13}C_2$–H coupling constants of di-*n*-butylvinylboronate (**1**) were 158 and 164 Hz, indicating that the C_2 has a normal sp^2 hybridization. The coupling constant of di-*n*-butylacetyleneboronate (**6**) was 240 Hz, demonstrating that the C_2 has a normal sp hybridization. The $^{13}C_2$–H coupling constant of *n*-butylboronate (**9**) was 124 Hz, indicating here also that the C_2 has a normal sp^3 hybridization.