Studies on *s-Cis/s-Trans* Preference of Acyclic α,β-Unsaturated Esters. Reactions, Supersonic Jet Spectroscopy, NOEs, and X-ray Analysis

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The *s-cis/s-trans* preference of acyclic α,β-unsaturated esters has been studied by their reactions to elucidate the preference in the transition state and by supersonic jet spectroscopy, NOE experiments, and X-ray analysis to clarify the preference in the ground state. It has been widely accepted that enoate–Lewis acid complexes prefer the *s-trans* conformation not only in the ground state but also in the transition state of the reactions involving those complexes. The conjugate addition of metal amides to uncomplexed enoates proceeds predominantly through the *s-cis* conformation, and most organocopper conjugate additions in the absence of Lewis acids or related metal salts take place preferentially in the *s-cis* conformation. It is clarified that the relative population of the *s-cis* and *s-trans* conformer of uncomplexed methyl cinnamate is nearly 1:1 in a supersonic free jet and in solution at room temperature. X-ray analyses of **23** and **24** indicate the *s-cis* conformation, suggesting that most enoates adopt the *s-cis* form in the solid state except for **16–18**.

Introduction

Asymmetric Diels–Alder, Michael addition, and ene reactions of acyclic α,β-unsaturated esters are one of the most fundamental processes in organic synthesis. The stereoselectivities and sense of chiral induction in these reactions depend strongly upon the conformation of acyclic α,β-unsaturated esters, namely the *s-cis/s-trans* preference of the enoates. It is generally accepted that Lewis acid complexation of enoates dramatically stabilizes the *s-trans* conformation relative to the *s-cis* by either electronic or steric effects.[1] Actually, the BF_3·OEt_2- or Me_3SiI-mediated organocopper conjugate additions,[2,3] Lewis acid-promoted Diels–Alder reactions,[3,4] and Et_2-AlCl-mediated ene reactions[5] provided predominantly or exclusively the products which were expected to be obtained from the reaction proceeding via the *s-trans* arrangement of the enoates. However, $TiCl_4$-[4g,6ab] or $EtAlCl_2$[6c]-mediated Diels–Alder reactions of certain enoates[4g,6] and enamides[7] proceeded via the *s-cis* conformation, primarily because of the result of the bidentate chelated geometry of the Lewis acid–ester (or amide) complexes. Thus, the *s-cis/s-trans* preference in the transition state is elucidated by the product stereochemistry. The ground-state conformations of enoate–Lewis acid complexes have been clarified by X-ray analysis, NMR, and IR methods. Evidence for the *s-trans* conformational preference of Lewis acid complexed enoates comes from the crystal structure of an (ethyl cinnamate)$_2$–$SnCl_4$ complex,[8] ^1H NMR chemical shifts of (8-phenylmenthyl acrylate)–$TiCl_4$ complex,[4a] and other spectroscopic studies,[9] whereas the crystal structure of a $TiCl_4$ complex of an acrylate of ethyl lactate indicates the *s-cis* arrangement.[4g] In conclusion, α,β-unsaturated ester–Lewis acid complexes prefer the *s-trans* conformation not only in the ground state but also in the transition state, except for the complexes of certain chiral acrylates[4g,6,7] in which bidentate Lewis acids coordinate a carbonyl oxygen of the enoate and an oxygen atom of a chiral auxiliary.[10]

On the other hand, the conformational preference of uncomplexed enoates is not straightforward. Ab initio

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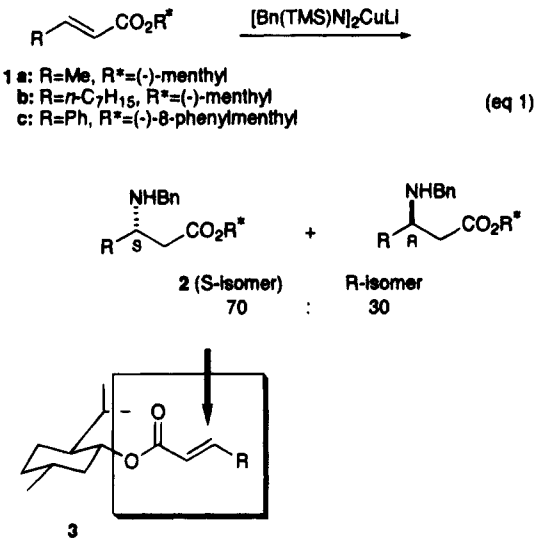
calculations have shown that the *s-cis* conformation of uncomplexed acrylates is slightly favored over the *s-trans* conformation,[1] suggesting that, for example, uncatalyzed Diels–Alder reactions may proceed via the *s-cis* conformation of the acrylate, or with little preference. The products which are expected from the reaction proceeding through the *s-cis* conformation have been obtained in the Michael addition of organocopper[11] and lithium amide reagents,[3,12] whereas products proceeding via the *s-trans* geometry have been afforded in organocopper[13] and amine[14] conjugate additions to similar enoates and in Diels–Alder reactions.[15] Evidence for the *s-cis* preference of a significant number of enoates has been obtained by X-ray analysis.[16] However, X-ray diffraction of three enoates has indicated the *s-trans* conformation.[17]

The *s-cis* conformation of methyl acrylate is found to be favored in the gas phase,[18] although IR spectroscopy in solution indicates that the *s-trans* conformer is the more stable.[9a,b] This reversal of the preferred conformation in solution has been rationalized by consideration of the dipole moments.[1] The *s-trans*,syn and *s-cis*,syn conformers have dipole moments of 2.55 and 1.65 D, respectively. Accordingly, the former should be stabilized to a larger extent than the latter in the liquid state or in a polar solvent. Thus, electrostatic interactions in solution displace the *s-cis*/*s-trans* equilibrium toward the *s-trans* conformation.[1]

Previous experimental results on the *s-cis*/*s-trans* conformational preference of uncomplexed α,β-unsaturated esters are summarized as follows: (1) most of the X-ray analysis data of enoates indicate a *s-cis* preference, except for three cases, and (2) studies based on IR spectroscopy in solution show a *s-trans* preference of methyl acrylate, although the *s-cis* conformation is favored in the gas phase. We report herein that (1) conjugate addition to uncomplexed α,β-unsaturated esters proceeds predominantly through the *s-cis* conformation, (2) the laser-induced fluorescence spectroscopy of jet-cooled methyl cinnamate indicates that the relative populations of the *s-cis* and *s-trans* conformers are almost equal in the isolated molecule at very low temperatures, (3) NOE experiments of methyl cinnamate show a slight preference for the *s-cis* form in solution at room and low temperatures, and (4) X-ray analyses of some key enoates further indicate the *s-cis* preference in the solid state.

Results and Discussion

1. Conjugate Additions, Diels–Alder Reactions, and Ene Reactions. The *s-cis*/*s-trans* preference of enoates at the transition state has been investigated by conjugate addition, Diels–Alder, and ene reactions. The addition of the copper–amide reagent $[Bn(TMS)N]_2CuLi$ to **1a** in the absence of Lewis acids gave a 70:30 mixture of **2** (*S*-isomer) and its *R*-isomer in 85% yield (eq 1).[19]



However, the high-pressure-mediated addition of Ph_2CHNH_2 to **1a** proceeded predominantly via the *s-trans* conformation.[14] The addition of the copper amide to **1b** afforded a similar result; the *S*-isomer was produced predominantly. These results clearly indicate that the addition of the copper amide proceeds predominantly through the *s-cis* conformation **3**. The addition of the lithium amide reagent (LSA) to **4** gave a 95:5 mixture of **5** (*S*-isomer) and its *R*-isomer in 95% yield (eq 2).[3] Here again, the addition proceeds through the *s-cis* conformation.[5] Furthermore, the addition of $[Bn(TMS)N]_2CuLi$ to **6** and **7** produced **8** and **9**, respectively, with high diastereoselectivities in high chemical yields.[12] Since **8** (*R*-isomer) is obtained from **6**, the addition takes place

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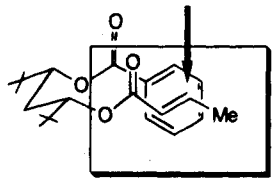
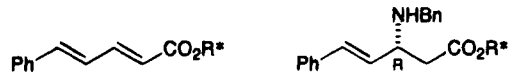
4: R*=3-(benzoyloxy)-2,2,6,6-tetramethyl-5-heptyl 5 (S-isomer) + R isomer 95 : 5

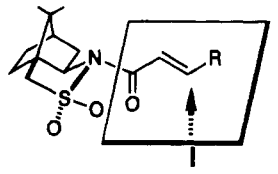


(eq 2)

via the *s-cis* geometry of the (−)-8-phenylmethyl ester **6** (see the *s-cis* form of the related (−)-menthyl ester **4**). The formation of **9** from **7** indicates that the addition proceeds through the *s-cis* conformation **10** of the camphor sultam derivative.[20] Accordingly, it is concluded that the conjugate addition of metal amides takes place predominantly on the *s-cis* conformation.



6: R*=(-)-8-phenylmenthyl
7: R*=(-)-D-camphor sultam
8: R*=(-)-8-phenylmenthyl
9: R*=(-)-D-camphor sultam



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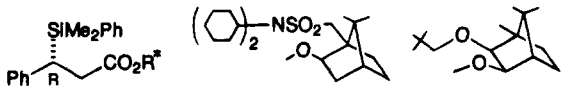
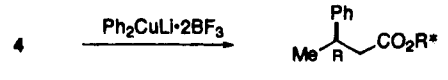
Conjugate addition of the higher order (phenyldimethylsilyl)cuprate $(PhMe_2Si)_2Cu(CN)Li_2$ to **1c** having a (−)-8-phenylmenthyl chiral auxiliary afforded a 60:40 mixture of **11** (*R*-isomer) and its *S*-isomer in 82% yield.[11b] The major product **11** is obtained via the attack of the reagent to the re face of the double bond of the *s-cis* conformer (see **3**). The cinnamate esters having other chiral auxiliaries **12** and **13** also gave the *R*-isomers



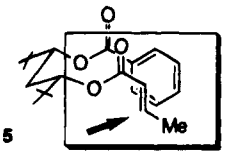
11: R*=(-)-8-phenylmenthyl 12 13

predominantly upon treatment with the higher order cyanocuprate, indicating that the conjugate addition takes place predominantly at the *s-cis* conformation. The conjugate addition of Bu_3CuLi_2 to 2-*exo*-bornyl crotonates proceeded through the *s-cis* conformation.[11a] On the other hand, as mentioned above, the organocopper conjugate addition in the presence of Lewis acids such as BF_3·OEt_2, Me_3SiI, and MgX_2 affords predominantly or exclusively the products which are produced from the reaction proceeding via the *s-trans* conformation.[2,3] For example, the addition of Ph_2CuLi·$2BF_3$·OEt_2 to **4** gave **14** with high diastereoselectivity, indicating that the reaction proceeded via the *s-trans* conformation **15**.[3] Consequently, it seems that the organocopper conjugate addition proceeds predominantly through the *s-cis* conformation in the absence of Lewis acids, salts (MX), or gegen cations (M^+) which can coordinate a carbonyl oxygen of enoates.[11]



14

(eq 3)



15

Most asymmetric Diels–Alder reactions of α,β-unsaturated esters bearing chiral auxiliaries have been carried out in the presence of Lewis acids or related additives[3,4,15] and thus have afforded the products, with high diastereoselectivities, which are expected from the reaction proceeding via the *s-trans* conformation. Therefore, the *s-cis/s-trans* problem is more straightforward in Diels–Alder reactions in comparison with organocopper conjugate additions. Perhaps one of the factors which complicate the issue in the case of organocopper conjugate additions is that the salts (MX) such as LiX and MgX_2 coexist, not always but very frequently, in the reaction system even in the absence of external additives.[21] Such salts may coordinate a carbonyl oxygen of enoates to stabilize the *s-trans* relative to the *s-cis* conformation. The Me_2AlCl-promoted intramolecular ene-type reaction of a (−)-8-phenylmenthyl enoate proceeded via the *s-trans* conformation.[5] Since the assistance of Lewis acids is needed in general, the *s-cis/s-trans* problem in ene reactions is straightforward; the *s-trans* conformation is involved at the transition state.

2. Laser Induced Fluorescence Spectroscopy of Jet-Cooled Methyl Cinnamate. Up to now, a variety of spectroscopic methods have been employed to investigate stable structures for alkyl-,[22a] (hydroxymethyl)-,[22c] methoxy-,[22d] amino-,[22e] and (aminomethyl)benzenes[22f] in supersonic jets. In the present experiment, measurements of laser-induced fluorescence spectra and dispersed fluorescence spectra of the S_1–S_0 transition were performed for supersonically cooled molecules. To help clarify the *s-cis/s-trans* preference of acyclic α,β-unsaturated esters, we chose methyl cinnamate (C_6H_5CH=$CHCO_2$-CH_3).

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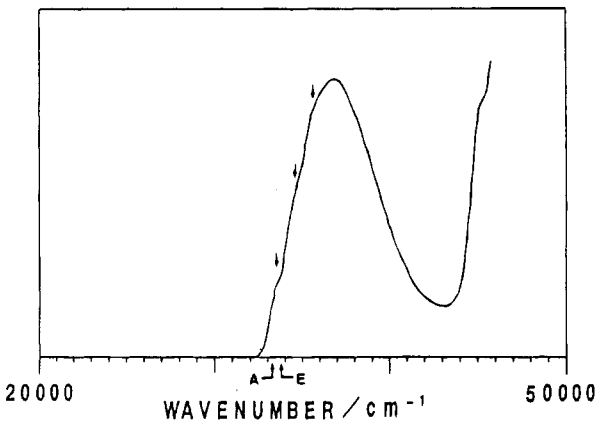


Figure 1. Absorption spectrum of methyl cinnamate in cyclohexane. Vibrational progression of 1100 cm^{-1} interval is marked in the spectrum (see text). A and E correspond to the positions of the peaks observed in the supersonic jet (see Figure 2).

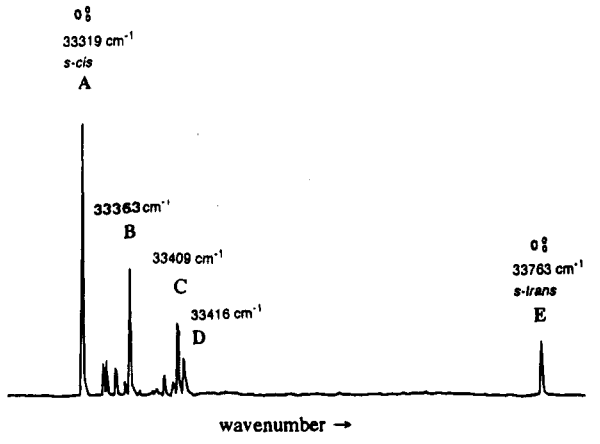


Figure 2. Fluorescence excitation spectrum of jet-cooled *s-cis* formof methyl cinnamate around its 0_0^0 transition regions.

First, the absorption spectrum of methyl cinnamate was measured in cyclohexane solution (Figure 1) to find the approximate origin of the S_1-S_0 transition. The band origin was determined roughly to be 300 nm (33 300 cm^{-1}). As can be seen in Figure 1, a vibrational structure with 1100 cm^{-1} spacing is observed in the spectrum. This vibration is assigned to the CO stretching vibration of the carbonyl group in S_1. Figure 2 shows the corresponding laser-induced fluorescence excitation spectrum of the jet-cooled methyl cinnamate. As can be seen in Figure 2, peak A at 33 319 cm^{-1} is assigned to the band origin of this molecule. In the first 100 cm^{-1} energy region above the band origin, many bands which may be assigned to the torsional vibration of the phenyl group in the S_1 state are observed. Figures 3–6 show the dispersed fluorescence spectra for those bands. Table 1 lists the energies of the vibrational bands observed in the dispersed fluorescence spectrum of peak A. The vibration of 1642 cm^{-1} energy is assigned to the CO stretching vibration of the carbonyl group in S_1. The appearance of the CO stretching vibration in addition to the vibrational bands of the phenyl group means that the S_1 state has both the $n\pi^*$ transition character of a carbonyl group and the $\pi\pi^*$ character of a phenyl group.

We then measured the dispersed fluorescence spectrum of the peak E which is located 444 cm^{-1} to the higher energy side of peak A in Figure 2. Figure 7 shows the dispersed fluorescence spectrum of peak E, and the energies of the vibrational bands observed in the dispersed fluorescence spectrum are shown in Table 2. As can be seen in Figure 7, the spectrum shows a vibrational structure similar to that of the fluorescence spectrum of peak A (Figure 3). Therefore, peak E cannot be assigned to the vibronic bands belonging to peak A and rather can be assigned to the band origin of another conformer of methyl cinnamate. That is, peaks A and E are assigned to the band origins of different conformers of methyl cinnamate, the *s-cis/s-trans* conformers. Hereafter, peak A corresponds to conformer A and peak E to conformer E. The appearance of low-frequency torsional vibrations around peak A indicates that the structural deformation of conformer A from S_0 to S_1 is larger than that of conformer E.[24] The difference of the barrier of the torsional motion of phenyl group may be due to the difference in the interaction between the O atom of the carbonyl group and phenyl group. Since the distance between the carbonyl oxygen atom and phenyl group is shorter in the *s-cis* conformer than in the *s-trans* conformer, the torsional barrier of the *s-cis* conformer may be more affected than the *s-trans* conformer. Therefore, peak A is assigned tentatively to the *s-cis* form and peak E is assigned to the *s-trans* form, although these assignments are highly speculative.

In general, the conversion between conformers during the supersonic expansion is negligibly small and the relative populations of the conformers in a jet is not very different from that of the conformers at room temperature.[22h] To determine the relative populations of the *s-cis/s-trans* conformers from the fluorescence excitation spectra in the jet, it is necessary to know the relative absorption cross sections and fluorescence quantum

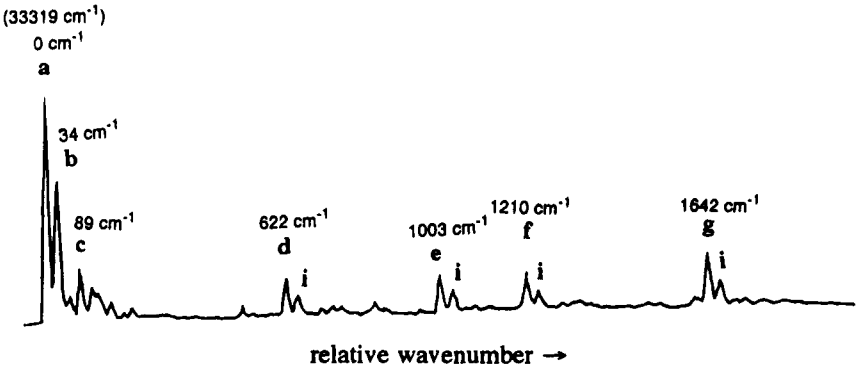


Figure 3. Dispersed emission spectrum of *s-cis* form of methyl cinnamate excited at 33 319 cm^{-1}, the feature marked A in Figure 2.

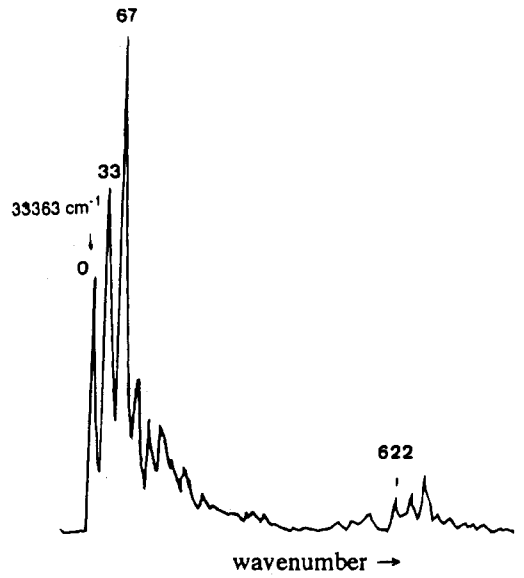


Figure 4. Dispersed emission spectrum of s-cis form of methyl cinnamate excited at 33 363 cm^{-1}, the feature marked B in Figure 2.

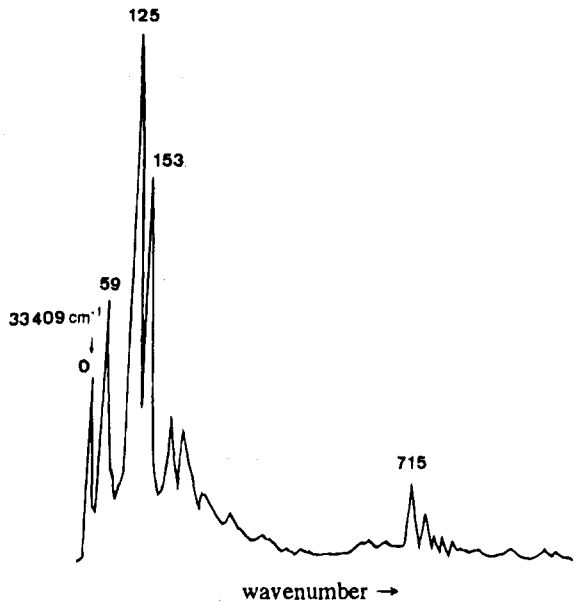


Figure 5. Dispersed emission spectrum of s-cis form of methyl cinnamate excited at 33 409 cm^{-1}, the feature marked C in Figure 2.

yields. The absorption cross section may not be different between the two conformers. On the other hand, it was found that the fluorescence quantum yield was quite different between the conformers from the measurement of fluorescence lifetimes. The fluorescence lifetime for the s-cis conformer (peak A) was determined to be 17 ± 3 ns, while that of the *s-trans* conformer (peak E) was estimated to be shorter than 2 ns. So, the ratio of the fluorescence quantum yields for the *s-trans/s-cis* conformers is equal to or larger than 0.11. In the LIF spectrum of Figure 2, the ratio of the integrated LIF intensities of the *s-trans/s-cis* conformers is approximately 0.1. From these results, we obtain the relative populations of *s-trans/s-cis* ≥ 0.8 in the jet. On the other hand, the relative intensities at the position of peak E (33 763 cm^{-1}) to that of peak A (33 319 cm^{-1}) in the absorption spectrum of Figure 1 is 1.3. Since the difference in the absorption cross sections between the two conformers is small, this value is almost equal to the relative population ratio. Therefore, in due consideration of the uncertainties of the above estimation, it is concluded that the populations of the two conformers are almost equal. Accordingly, the assignments which we made to peak A and peak E are not so important: even if our assignments were reversed, the final conclusion does not change.

(24) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5039.

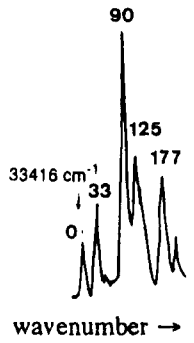


Figure 6. Dispersed emission spectrum of s-cis form of methyl cinnamate excited at 33 416 cm^{-1}, the feature marked D in Figure 2.

Table 1. Vibrational Bands Observed in the Dispersed Fluorescence Spectrum of Peak A

feature[a]	ν-ν_0^0, cm^{-1}	assignment[b]
a	0 (33 319)	origin
b	34	T
c	89	T
d	622	6b
e	1003	12
f	1210	9b
g	1642	S

[a] The features a–g are the notations used in Figure 3 for the observed vibronic features in the dispersed emission spectrum of methyl cinnamate. [b] The notations of 6b, 12, and 9b are the normal vibrational motions of the benzene ring,[23] T is the notation for the torsional vibrational motion, and S is the notation for the stretching vibrational motion of carbonyl group.

Next, we compared the dispersed emission spectrum in a supersonic free jet of the *s-cis* form excited at 33 319 cm^{-1} (0_0^0 transition, Figure 3) or the *s-trans* form excited at 33 763 cm^{-1} (0_0^0 transition, Figure 4) with the infrared spectrum of methyl cinnamate in CCl_4. The data are shown in Figure 8 and Table 3. There is a good correspondence between the dispersed emission spectroscopy in a supersonic free jet and the infrared spectroscopy of methyl cinnamate.

3. NOE Experiments of Methyl Cinnamate. When the methyl protons (δ 3.81 in $CDCl_3$) of methyl cinnamate were irradiated at room temperature, NOEs were observed at both H_α (28%) and H_β (26%) protons At −60 °C, signal enhancement at H_α and H_β became 31 and 27%, respectively. Therefore, the enhancement slightly increased at lower temperatures more at the H_α proton than at the H_β proton. It is reasonable to assume that the H_α proton is enhanced primarily when methyl cinnamate adopts the *s-cis*,anti form and that the enhancement is very weak or negligible when it adopts the *s-cis*,syn or the *s-trans* conformations. Quite similarly, it is presumed that the enhancement at the H_β proton is primarily attributed to the intervention of the *s-trans*,-anti conformation. Accordingly, it is concluded that the *s-cis* form is favored very slightly over the *s-trans* form

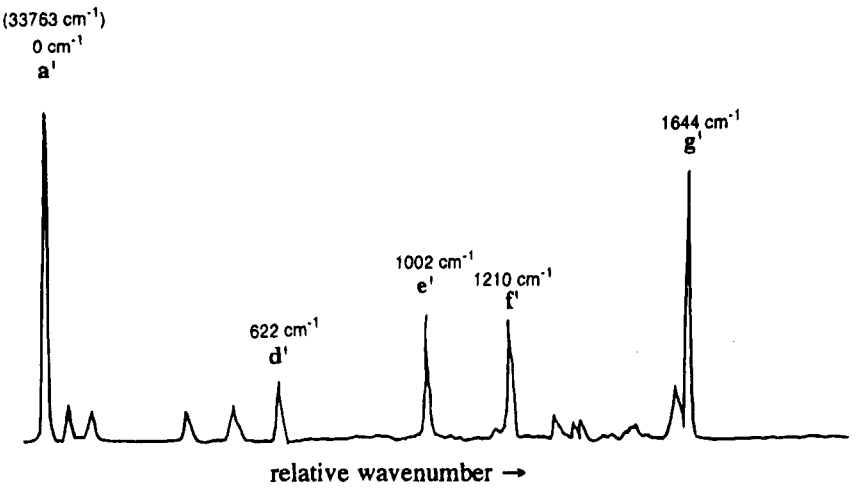


Figure 7. Dispersed emission spectrum of s-trans form of methyl cinnamate excited at 33 763 cm^{-1}, the feature marked E in Figure 2.

Table 2. Vibrational Bands Observed in the Dispersed Fluorescence Spectrum of Peak E

feature[a]	ν-ν (0_0^0), cm^{-1}	assignment[b]
a'	0 (33 763)	origin
d'	622	6b
e'	1002	12
f'	1210	9b
g'	1644	S

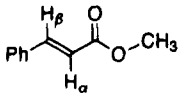
[a] The features a'–g' are the notations used in Figure 4 for the observed vibronic features in the dispersed emission spectrum of methyl cinnamate. [b] The notations of 6b, 12, and 9b are the normal vibrational motions of the benzene ring,[23] and S is the notation for the stretching vibrational motion of the carbonyl group.

Table 3. Vibronic Motion of Methyl Cinnamate

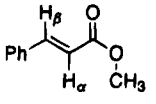
	wavenumber/cm^{-1}		
feature[a]	IR (Figure 8)	*s-cis* (Figure 3)	*s-trans* (Figure 4)
d''	629	622	622
e''	1007	1003	1002
f''	1203	1210	1210
g''	1639	1642	1644

[a] The features d''–g'' are the notations used in Figure 8 for the observed vibronic features in the infrared spectrum of methyl cinnamate.

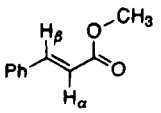
in solution, since enhancement at the H_α proton increased more at lower temperatures than that at the H_β proton..



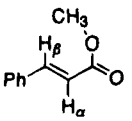
s-cis, syn



s-cis, anti

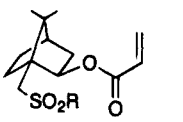


s-trans, syn

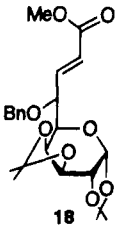


s-trans, anti

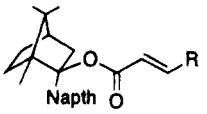
4. X-ray Analysis. As mentioned in the Introduction, only three enoates[17] (**16**–**18**) have been found to adopt the *s-trans* conformation in the solid state whereas all the remaining enoates adopt the *s-cis* conformation.[16] For example, X-ray analysis of **19**–**21**, which are structually similar to **16** and **17**,[15d,e] indicates the *s-cis* conformation. The *trans*-isomer **18** adopts the *s-trans* conformation,[16l] although the *cis*-isomer **22** prefers the *s-cis* geometry.[16l] We thought that the functional group (SO_2R) and/or the double bond geometry (trans and cis in **18** and **22**, respectively) might play an important role to control the *s-cis*/*s-trans* preference in the solid state. Accordingly, we carried out X-ray analyses of **23** and **24**, and the crystal structures are shown in Figure 9 and 10. Some selected torsion angles (**A**–**C**) are summarized in Table 4. The number labeled at each atom shown in Table 4



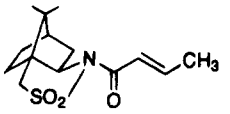
16: R = $N(C_6H_{11})_2$
17: R = Ph



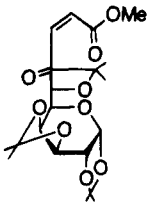
18



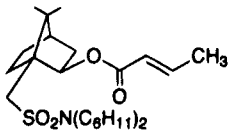
19: R = H
20: R = CH_3



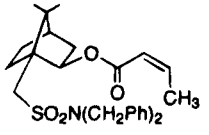
21



22



23



24

corresponds to that of the X-ray structure. Torsion angle

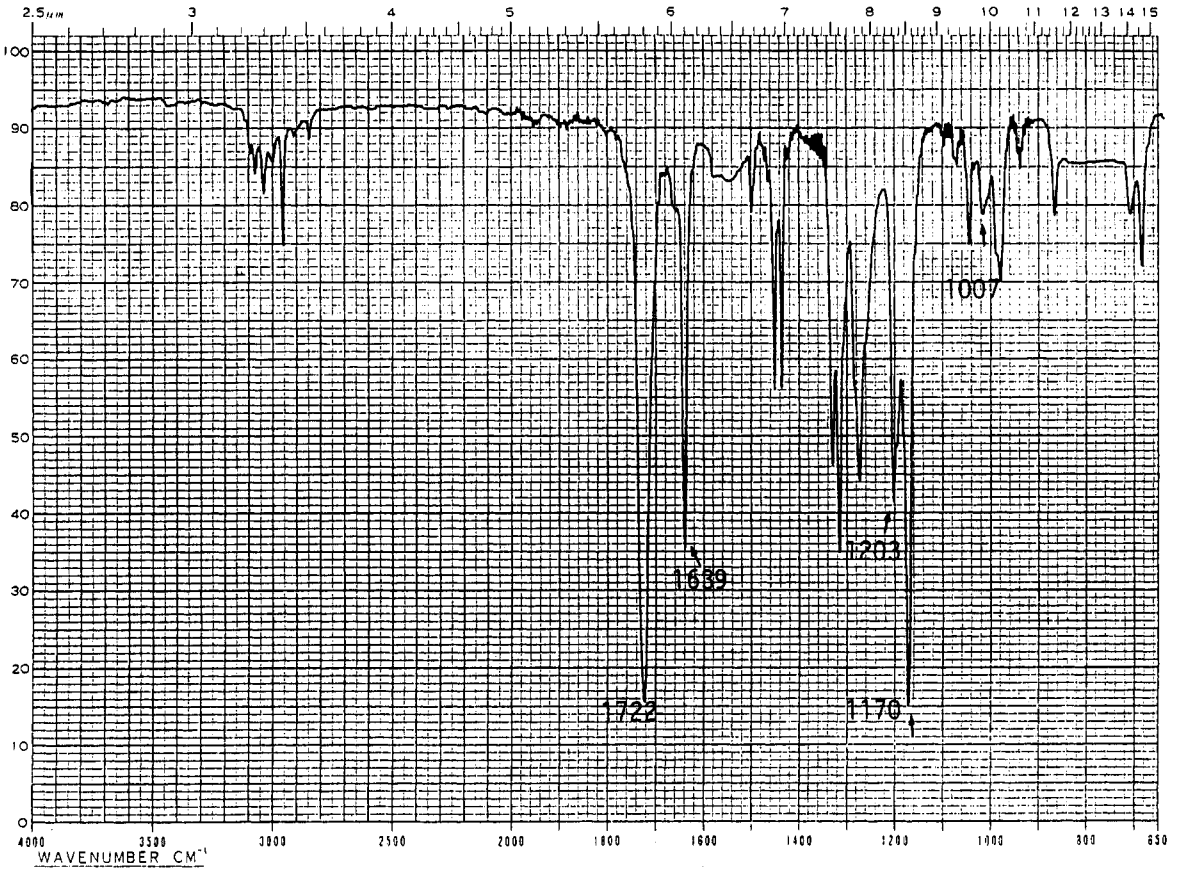


Figure 8. Infrared spectrum of methyl cinnamate (CCl_4).

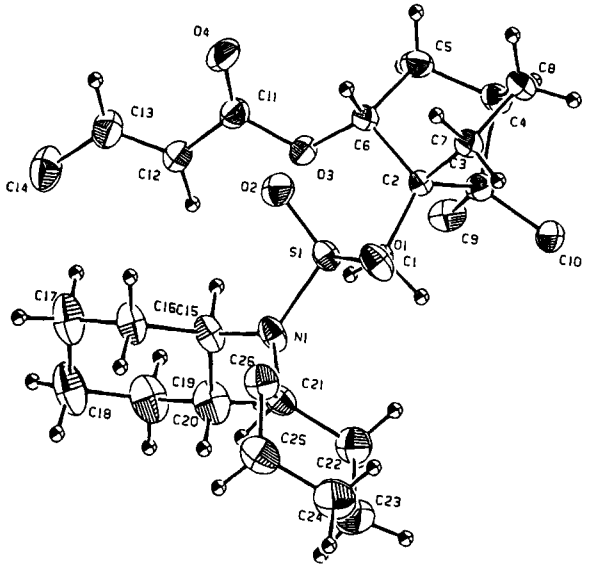


Figure 9. ORTEP drawing of (+)-10-[(dicyclohexylamino)-sulfonyl]born-6-yl 2(*E*)-butenoate (**23**).

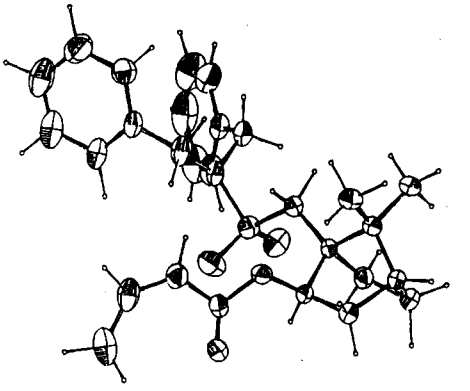


Figure 10. ORTEP drawing of (+)-10-[(dibenzylamino)-sulfonyl]born-6-yl 2(*Z*)-butenoate (**24**).

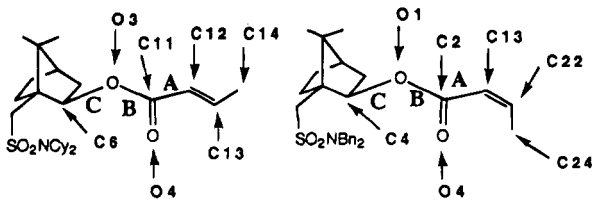
A is 5.90° in the case of **23** and −0.6° in case of **24**, clearly indicating the planar *s-cis* geometry. Torsion angle B is 1.0° in **23** and 6.1° in **24**, whereas C is 27.5° in **23** and 18.8° in **24**, indicating the planar or nearly planar geometry of the CH—O—CO (ester) unit. Consequently, it seems that the *s-trans* preference in the cases of **16**–**18** represents rather special cases in the solid state, presumably due to unclarified crystal packing forces.

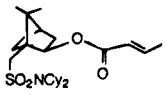
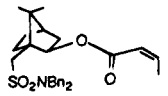
Conclusions. Previous computations for isolated uncomplexed methyl acrylate predicted that the *s-cis* conformation is more stable than the *s-trans* conformation.[1a] The conjugate addition of metal amides to α,β-unsaturated esters proceeds through the *s-cis* conformation, and the organocopper conjugate addition to uncomplexed enoates generally takes place via the *s-cis* form. We have clarified with experimental data that, for isolated methyl cinnamate in the gas phase at nearly 4 K, the relative populations of the *s-cis* and *s-trans* conformers are nearly 1:1 and that methyl cinnamate in solution adopts the *s-cis* form with a very slight preference over the *s-trans* form. Furthermore, X-ray analysis indicates that **23** and **24** adopt the *s-cis* conformation in the solid state, whereas it has been reported that **16** and **17** adopt the *s-trans* geometry.

Experimental Section

Preparation of (+)-10-[(Dibenzylamino)sulfonyl]born-6-yl 2-Butenoates (24). A 300-mL flame-dried, three-necked,

Table 4. Torsion Angles of Enoates 23 and 24 via X-ray Results[a]



substrate	torsion	torsion angle
	A (O4-C11-C12-C13)	5.9
	B (O4-C11-O3-C6)	1.0
	C (C11-O3-C6-H6)	27.5
	A (O4-C2-C13-C22)	-0.6
	B (O4-C2-O1-C4)	6.1
	C (C2-O1-C4-H4)	18.7

[a] Units: bond angle (deg).

round-bottom flask, equipped with a magnetic stirring bar was fitted with a rubber septum and a three-way stopcock under argon. The apparatus was charged with 7.007 g (16.9 mmol) of (+)-10-[(dibenzylamino)sulfonyl]bornan-6-ol dissolved in 115 mL of benzene. To the stirred solution were added 3.173 g (23.7 mmol) of silver cyanide and 3.239 mL (33.8 mmol) of crotonyl chloride. After being heated under reflux for 15 h, the reaction mixture was allowed to cool to 0 °C and then quenched by the addition of 2 M aqueous sodium hydroxide and diluted with benzene. The resulting mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with three portions of benzene. The organic layers were combined, washed with 10% aqueous citric acid and saturated brine, and dried over anhydrous potassium carbonate. The solvent was removed in vacuo, and the chromatography of the C resulting product on silica gel (450 g, 12:1 hexane/ethyl acetate) gave (+)-10-[(dibenzylamino)sulfonyl]born-6-yl 2(*E*)-butenoate as colorless needles (6.043 g, 74%) and its geometric isomer (+)-10-[(dibenzylamino)sulfonyl]born-6-yl 2(*Z*)-butenoate (691 mg, 8%) as colorless needles. (+)-10-[(Dibenzylamino)sulfonyl]-born-6-yl 2(*E*)-butenoate: colorless needles; mp 91 °C; $[\alpha]^{22}_D$ +1.39° (*c* 1.01, $CHCl_3$); IR (CCl_4) 3050, 3030, 2940, 1710, 1650, 1440, 1330, 1260, 1170, 1140, 1040, and 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.39–7.27 (10 H, m), 6.87 (1 H, dq, *J* = 15.7 and 6.9 Hz), 5.77 (1 H, dq, *J* = 15.7 and 1.8 Hz), 5.01 (1 H, m), 4.31 (2 H, broad), 4.30 (2 H, broad), 3.29 (1 H, d, *J* = 13.5 Hz), 2.62 (1 H, d, *J* = 13.5 Hz), 1.96 (2 H, m), 1.76 (3 H, dd *J* = 6.9 and 1.8 Hz), 1.81–1.60 (4 H, m), 1.26 (1 H, m), 0.94 (3 H, s), and 0.80 (3 H, s). Anal. Found: C, 69.97; H, 7.30; N, 2.88; S, 6.73. Calcd for $C_{28}H_{35}NO_4S$: C, 69.82; H, 7.32; N, 2.91; S, 6.66%. (+)-10-[(Dibenzylamino)sulfonyl]born-6-yl 2(*Z*)-butenoate: colorless needles; mp 177 °C; $[\alpha]^{25}_D$ +10.20° (*c* 1.05, $CHCl_3$); IR (CCl_4) 3030, 2950, 1720, 1340, 1190, 1150, 1060, and 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.39–7.27 (10 H, m), 6.23 (1 H, dq, *J* = 11.4 and 7.4 Hz), 5.72 (1 H, dq, *J* = 11.4 and 1.8 Hz), 5.04 (1 H, dd, *J* = 7.5 and 3.0 Hz), 4.31 (4 H, broads), 3.22 (1 H, d, *J* = 13.4 Hz), 2.59 (1 H, d, *J* = 13.4 Hz), 2.27 (3 H, dd, *J* = 7.4 and 1.8 Hz), 2.04–1.88 (2 H, m), 1.82–1.61 (4 H, m), 1.22 (1 H, m), 0.93 (3 H, s), and 0.79 (3 H, s). Anal. Found: C, 70.13; H, 7.31; N, 2.99; S, 6.43. Calcd for $C_{28}H_{35}NO_4S$: C, 69.82; H, 7.32; N, 2.91; S, 6.66.

Preparation of (+)-10-[(Dibenzylamino)sulfonyl]-bornan-6-one. A 200-mL two-necked, round-bottom flask, equipped with a magnetic stirring bar, was fitted with a calcium chloride drying tube and a dropping funnel. The apparatus was charged with 672 mg (5.5 mmol) of (dimethylamino)pyridine dissolved in 28 mL of dimethylformamide. To the stirred solution was added 10.6 mL (55 mmol) of dibenzylamine and 6.46 mL of (55 mmol) of isoquinoline. Then the apparatus was cooled to 0 °C, 7.02 g (28 mmol) of (+)-camphor-10-sulfonyl chloride was added dropwise over 1 h. After being stirred at 0 ×b0°C for 1 h, the reaction mixture was quenched by the addition of 10% aqueous citric acid and diluted with dichloromethane. The resulting mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with three portions of dichloromethane. The usual workup gave (+)-10-[(dibenzylamino)sulfonyl]bornan-6-one (8.923 g, 78%) as colorless needles: mp 78 °×b0C; $[\alpha]^{23}_D$ +34.510° (*c* 1.095, $CHCl_3$); IR (CCl_4) 3030, 2960, 1740, 1340, 1150, 1050, and 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.36–7.28 (10 H, m), 4.47 (2 H, d, *J* = 15.0 Hz), 4.30 (2 H, d, *J* = 15.0 Hz), 3.29 (1 H, d, *J* = 14.5 Hz), 2.62 (1 H, d, *J* = 14.5 Hz), 2.57 (1 H, m), 2.35 (1 H, ddd, *J* = 18.0, 4.0, and 8.5 Hz), 2.08 (1 H, ddd, *J* = 4.0, 5.0, and 8.5 Hz), 2.22(1 H, m), 1.93 (1 H, d, *J* = 18.0 Hz), 1.68 (1 H, ddd, *J* = 13.6, 9.5, and 4.0 Hz), 1.42 (1 H, m), 1.12 (3 H, s), and 0.78 (3 H, s). Anal. Found: C, 70.25; H, 7.10; N, 3.49; S, 7.92. Calcd for $C_{24}H_{29}NO_3S$: C, 70.40; H, 7.10; N, 3.40; S, 7.79.

Preparation of (+)-10-[(Dibenzylamino)sulfonyl]-bornan-6-ol. A 300-mL flame-dried, three-necked, round-bottom flask, equipped with a magnetic stirring bar, was fitted with a rubber septum, a dropping funnel, and a three-way stopcock under argon. The apparatus was charged with 8.807 g (19.6 mmol) of (+)-10-[(dibenzylamino)sulfonyl]bornan-6-one dissolved in 30 mL of tetrahydrofuran. To the solution was added 21.6 mL (21.4 mmol of 1 M solution in tetrahydrofuran) of L-Selectride (Aldrich) dropwise over 20 min at −78 °C. After being stirred at −78 °C for 30 min, the mixture was allowed to warm at room temperature for 4.5 h. The reaction mixture was quenched by the successive addition of 4.65 mL of water slowly, 16.92 mL of ethanol, 22.56 mL of 3 M aqueous sodium hydroxide, and 16.92 mL of 30% aqueous hydroperoxide. The resulting mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with three portions of 3:1 ether/tetrahydrofuran. The organic layers were combined, washed with saturated brine, and dried over anhydrous magnesium sulfate. In vacuo removal of the solvent gave a solid. Recrystallization of the solid from hexane gave (+)-10-[(dibenzylamino)sulfonyl]-bornan-6-ol (7.450 g, 92%) as colorless needles. (+)-10-[(Dibenzylamino)sulfonyl]bornan-6-ol: colorless needles; mp 132 °C; $[\alpha]^{24}_D$ −31.827° (*c* 1.005, $CHCl_3$); IR (CCl_4) 3510, 3030, 2950, 1330, 1260, 1140, 1050, and 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.42-7.29 (10 H, m), 4.33 (2 H, broads), 4.32 (2 H, broad), 4.10 (1 H, dm, *J* = 3.5 Hz), 3.30 (1 H, d, *J* = 3.5 Hz), 3.12 (1 H, d, *J* = 13.5 Hz), 2.49 (1 H, d, *J* = 13.5 Hz), 1.78 (2 H, m), 1.69 (2 H, m), 1.65 (1 H, m), 1.57 (1 H, m), 1.12 (1 H, m), 0.95 (3 H, s), and 0.67 (3 H, s). Anal. Found: C, 69.85; H, 7.64; N, 3.39; S, 7.48. Calcd for $C_{24}H_{31}NO_3S$: C, 69,70; H, 7.56; N, 3.39; S, 7.75.

X-ray Analysis of 23 and 24. The author has deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Electronic Spectroscopy in a Supersonic Jet. The fluorescence excitation spectra and the dispersed fluorescence spectra of methyl cinnamate in a supersonic jet were measured by the conventional method. The sample was seeded in He carrier gas and expanded into a vacuum chamber through a pulsed nozzle. The exciting light was the second harmonic (KDP) of a dye laser pumped by a nitrogen laser. The laser resolution was about 1.0 cm^{-1} (FWHM). The dispersed fluorescence spectra were measured with a Nalimi 0.75-m grating spectrograph with a spectral resolution of 4 cm^{-1} (FWHM). The sample was heated up to about 310 K to obtain sufficient vapor pressure.