BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2558—2566 (1970)

Conformations of the Ester Group

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(Received February 16, 1970)

In some esters of formic acid which carry bulky alkyl groups (*e .g*, *t*-butyl formate, 1,1-diethylpropyl formate, and triphenylmethyl formate), the presence of *s-cis* conformer has been confirmed by various spectroscopic techniques. The dipole-moment measurements also support the conclusion drawn from the spectroscopic data.

It has been reported that the *s-cis* conformer as well as the *s-trans* conformer is present in many carboxylic acids[1–3] and amides.[4,5] The presence of these isomers can be attributed to the partial double bond character of the C–O or C–N bond due to delocalization of the electrons. Although the ester is an analogous compound, its conformation has been reported to be *s-trans*, chiefly on the basis of the results of dipole moment measurements[6] and microwave spectroscopy.[7,8] The *s-cis* conformer has only rarely been found.[9,10]

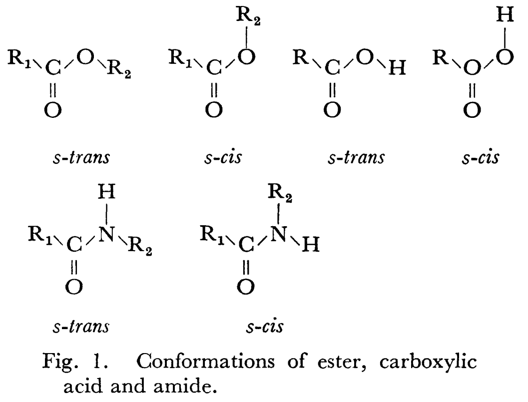
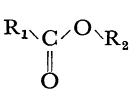


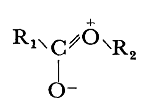
Fig. 1. Conformations of ester, carboxylic acid and amide.

However, it is well known that the C–O bond of



$R_1C(=O)OR_2$

Ia



$R_1C(O^-)=\overset{+}{O}R_2$

Ib

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1) M. Ōki and M. Hirota, *Nippon Kagaku Zasshi*, **81**, 855 (1960).

2) M. Ōki and M. Hirota, This Bulletin, **33**, 119 (1960).

3) M. Ōki and M. Hirota, *ibid.*, **34**, 374 (1961).

4) L. A. LaPlanche and M. T. Rogers, *J. Amer. Soc.*, **86**, 337 (1964).

5) H. Kessler and A. Rieker, *Ann. Chem.*, **708**, 57 (1967).

6) a) A. Euker and L. Meyer, *Z. Phys.*, **30**, 397 (1929). b) C. T. Zahn, *ibid.*, **33**, 70 (1952). c) L. Meyer, *Z. Phys. Chem. Ber.*, **8**, 27 (1930). d) J. M. Sturtevant, *J. Amer. Chem. Soc.*, **55**, 4478 (1933). e) C. T. Zahn, *Trans. Faraday. Soc.*, **30**, 804 (1934). f) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1936**, 1383. g) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

7) J. M. Ogorman, W. Schand, Jr., and V. Schomaker, *J. Amer. Chem. Soc.*, **72**, 4222 (1950).

8) R. F. Curl, *J. Chem. Phys.*, **30**, 1529 (1959).

9) B. Krishna, S. C. Srivastava and S. V. Mahadame, *Tetrahedron*, **23**, 4801 (1967). Krishna reported on the basis of dipole moment data that geranyl formate had the *s-cis* conformation, but there are not sufficient data to confirm the existence of the *s-cis* isomer.

10) D. N. Hall and J. Lamb, *Trans. Faraday Soc.*, **55**, 784 (1959).

the ester also has a partial double bond character due to the delocalization of electrons, as is exemplified by the resonance structures, (Ia, Ib). Therefore, *s-cis* conformers like carboxylic acid and amide may exist in some esters if either the *s-cis* conformer is stabilized or the *s-trans* is destabilized for some reason.

The purpose of this paper is to present the spectroscopic evidence, as well as the support from the dipole moment data, for the presence of *s-cis* conformers in some alkyl formates; it will also consider the effect of the bulkiness of the alkyl part of alkyl formates on the presence of the rotational isomers about the C–O bond of the esters.

Experimental

Materials. The simple esters were prepared by the standard methods. The *t*-butyl acetate was prepared from anhydrous acetic acid and *t*-butyl alcohol in the presence of zinc chloride. The *t*-butyl formate, *t*-amyl formate, 1-ethylpropyl formate, 1,1-diethylpropyl formate, phenyl formate, 2,6-dimethylphenyl formate, and geranyl formate were prepared from mixed anhydride of formic and acetic acid and the corresponding alcohol according to the Stevens method.[11] The triphenylmethyl formate was prepared from sodium formate and triphenylmethyl chloride.[12]

The γ-butyrolactone and cyclopentadecanolide were of commercial origin and were purified before the measurements.

The ε-caprolactone and cyclododecanolide were prepared from the corresponding ketone and perbenzoic acid. The physical constants of the compounds used in this study agree with those previously reported in the literature.

Apparatus. The IR spectra were measured by using a Perkin-Elmer 112G grating spectrometer, (1800—1700 cm^{-1}) (the precision of the instrument was believed to be 0.5 cm^{-1} at 1750 cm^{-1}), a JEOC-DS-402G infrared spectrophotometer (4000—400 cm^{-1}), a Hitachi EPI-G2 grating infrared spectrophotometer (1200—400 cm^{-1}), and a Hitachi EPI-L grating infrared spectrophotometer (700—200 cm^{-1}).

The UV spectra were measured on a Hitachi EPS-3 recording spectrophotometer.

The NMR spectra were measured on a JNM-C-60 spectrometer and on a JNM-4H-100 spectrometer.

The dipole moment was measured by the heterodine-beat method. (The estimated error was about 0.05D at 1.5D and about 0.02D at 2.5D).

Results and Discussion

The three chief factors governing the preference of the conformations of ester can be considered to be: the dipole-dipole interaction between C=O and O–R$_2$ bonds (Fig. 2a), the repulsion between lone-pair electrons of two oxygen atoms (Fig. 2b), and the steric repulsion either between C=O and R$_2$ or between R$_1$ and R$_2$ (Fig. 2c).

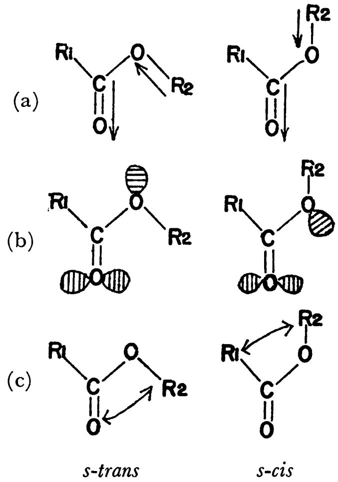

Fig. 2. The chief factors governing ester conformation.

The direction of the dipoles of the two bonds is roughly antiparallel in the *s-trans* conformer and roughly parallel in the *s-cis*. Therefore, the *s-trans* conformer is favored over the *s-cis* in less polar media as far as the first factor is concerned. In the second factor, the repulsion is considered to be very small in the *trans* conformer compared to that in the *s-cis*. Thus, the *s-trans* conformer is more stable than the *s-cis*. As to the third factor, when R$_1$ is bulky, the steric repulsion between C=O and R$_2$ in the *s-trans* conformer should be smaller than that between R$_1$ and R$_2$ found in the *s-cis*. Thus, the *s-trans* conformer is more stable in the ordinary esters. However, when R$_1$ is small, and R$_2$ bulky, the situation may be reversed; the *s-cis* conformer could be favored over the *s-trans* because of the increase in the interaction between R$_2$ and O relative to that between R$_1$ and R$_2$. These considerations lead to the conclusion that a *s-cis* conformer of the ester may exist when the ester has a small R$_1$ and a bulky R$_2$, which is possible in some formates which carry a large alkyl group.

Infrared Spectra

From the results obtained with carboxylic acids[13] and ketones,[14] it is natural to consider that the *s-cis* and *s-trans* conformations of the ester are reflected in the C=O stretching absorptions of these compounds. The results obtained with solutions in nonpolar solvents are shown in Table 1. It may be pointed out that some formates and acetates with

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[11] W. Stevens and A. van. Es, *Rec. Trav. Chim. Pays-Bas*, **83**, 1287 (1964).

[12] S. L. Fires, *J. Amer. Chem. Soc.*, **71**, 2571 (1949)

[13] M. Ōki and M. Hirota, This Bulletin, **34**, 374 (1961).

[14] M. Hirota, T. Hagiwara and H. Satonaka, *ibid.*, **40**, 2439 (1967).

Table 1. Absorption maxima due to carbonyl stretching vibration of esters (in CCl_4 or CS_2)

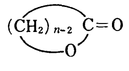
Compound	ν_{CO} (cm^{-1})	Compound	ν_{CO} (cm^{-1})
HCO_2CH_3	1733	$CH_3CO_2CH_3$	1749
$HCO_2C_2H_5$	1729	$CH_3CO_2C_2H_5$	1741
$HCO_2CH(CH_3)_2$	1725	$CH_3CO_2CH(CH_3)_2$	1737
$HCO_2C(CH_3)_3$	1722	$CH_3CO_2C(CH_3)_3$	1736
$HCO_2C(C_2H_5)_3$	1723		
$HCO_2C_{10}H_{17}$*	1728		

* geranyl formate

rather bulky alkyl groups show absorptions at the lower frequencies. However, this can not be taken as positive evidence for the presence of rotational isomers, because the absorption band is rather symmetrical except in the cases of isopropyl acetate and *t*-butyl acetate[*1] (see the discussions of the solvent effects). The present authors presume that the shift is the mere reflection of some effects of the electrical and bonding natures.

There are some lactones which are forced to take the *s-cis* conformation. Therefore, if the C=O absorption due to the lactones of the smaller ring and that due to the large lactone ring are compared, there will be a chance of finding the difference between the two conformers. Thus, the infrared C=O absorptions of various lactones were measured; the results are given in Table 2. The extraordinarily high frequency of γ-butyrolactone is, of course, attributable to the ring strain or the angle deviation, whereas ε-caprolactone is a compound which can take the *s-cis* conformation only. Judging from the knowledge of other esters, it may be assumed that cyclopentadecanolide exists in the *s-trans* conformation only. The data in Table 2 indicate that there is not much difference between these two compounds. Cyclododecanolide is expected to be a composite of *s-cis* and *s-trans* conformers, since the analogous C_{12} lactam is known to be so from NMR spectroscopy.[15] However, it shows only one sharp absorption in the carbonyl region. These results, although negative, may be interpreted as indicating that the *s-cis* and *s-trans* conformations of the ester can not be distinguished by the infrared C=O absorptions as measured in carbon tetrachloride or carbon disulfide.[16] Although the investigation of the infrared spectra in the C=O stretching region may not reveal the presence of the *s-cis* and *s-trans* conformers, the skeletal deformation region may be useful to this end, because the skeletal deformation is known to be sensitive to conformational change and because it has been shown recently that the spectra of amides in the 1200—200 cm^{-1} region reflect the presence of conformers superbly.[17]

Table 2. Absorption maxima due to carbonyl stretching vibration of lactones (in CCl_4)

n	Compound	ν_{CO} (cm^{-1})	
5	γ-butyrolactone	1783	
7	ε-caprolactone	1740	 $(CH_2)_{n-2}$ C=O O
13	cyclododecanolide	1736	
16	cyclopentadecanolide	1735	

The Effect of Temperature on the Absorptions in the 1200—200 cm^{-1} Region. The infrared spectra of *t*-butyl formate (II) were thus measured in various states and at various temperatures. The results are shown in Figs. 3 and 4.

Apparently, the intensities of absorptions bands change with a change in the temperature from 20°C (liquid) to <-100°C (solid), as is shown in Fig. 3;

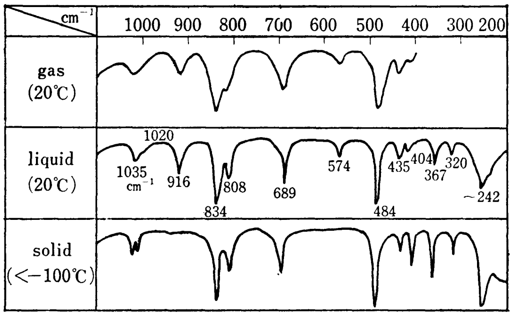


Fig. 3. IR spectra of *t*-butyl formate in three phases.

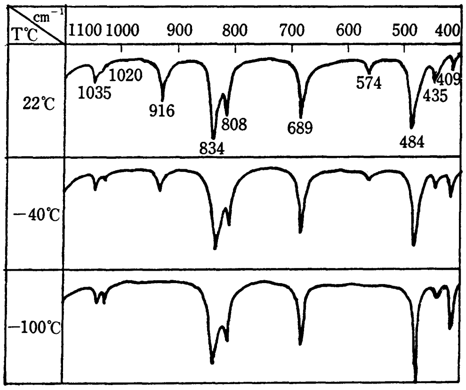


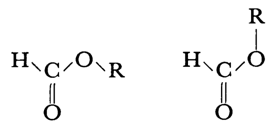
Fig. 4. Temperature change of IR spectra of *t*-butyl formate in liquid state.

[*1] In these acetates, the absorptions are unsymmetrical. Regarding this phenomena, an extensive discussion will be presented in subsequent papers.

15) R. M. Moriarty and J. M. Kliegman, *Tetrahedron Lett.*, **1966**, 891.

16) Owen and Sheppard could not find the *s-cis* conformer by means of the infrared spectra. N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, **1963**, 264.

17) Y. Koyama. the university of Tokyo, private communication.



s-trans *s-cis*

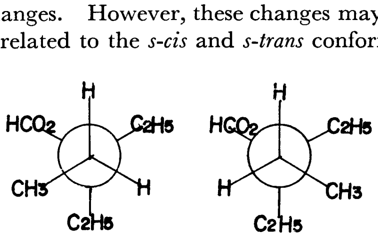
II: R=*t*-Bu
III: CEt_3
IV: $R=C_{10}H_{17}$ (geranyl)

for example, the absorptions at 916 cm^{-1} and 574 cm^{-1}, which are present at 20°C, disappear in the spectrum of the solid. In the gas phase at a lower pressure, the absorptions become broader than those in the liquid phase, although all the absorptions which are present in the liquid phase also exist in the spectra of the gas.

A temperature dependence (Fig. 4) study of the spectra of liquid *t*-butyl formate has shown the interesting features of some bands; the intensities of the bands at 916, 574, and 435 cm^{-1} decrease as the temperature is lowered, whereas those at 1020, 484, 409, and 242 cm^{-1} increase at low temperatures. The temperature dependence study of the spectra of gaseous *t*-butyl formate at 20—70°C reveals the same tendency. These phenomena may be explained by asuming the presence of conformational isomers. These studies alone not establish how many conformers are present, but, from the considerations of structure, it may now be said that *t*-butyl formate has two conformers, *s-cis* and *s-trans*, and that the populations of these isomers change as the temperature varies, and that these changes are reflected in the far-infrared spectra. It is not easy to assign these bands at the present time; further sutdy will be necessary to clarify this point.[18]

A far-infrared spectral study of 1,1-diethylpropyl formate (III) and geranyl formate (IV) was also carried out, because the former compound has a bulkier alkyl group than *t*-butyl formate, while the latter has been reported, on the basis of dipole moment data, to exist as an *s-cis* conformer.[9]

The spectra of these compounds measured under various conditions (gas, liquid, solid, and temperature range 81.0°C to −100°C) show very complicated changes. However, these changes may not be directly related to the *s-cis* and *s-trans* conformers of the ester group, because there are many rotational isomers possible for the alkyl part also. *t*-Butyl formate is simple in this respect; the only rotational axis considered is C_{co}–O_{ether}; rotation about the other axes produces the same conformation because of the symmetry of the substituent. 1,1-Diethylpropyl formate, on the other hand, has two different conformations (Va, Vb), in addition to the *s-cis* and *s-trans* conformers, because of rotation about the C–C axis of the ethyl group. There is no doubt about the presence of more possible conformers in geranyl formate. Although desirable, it was even impossible to correlate these spectra with those of *t*-butyl formate, because the absorptions are seriously shifted by the mass effect.



Va Vb

Solvent Effect in the 1200—400 cm^{-1} Region. The *s-cis* conformer of ester is considered to be more polar than the *s-trans*, judging from the arrangement of bond dipoles, and the dipole moments are calculated to be 3.04 and 1.53 D for the *s-cis* and *s-trans* conformers respectively. This implies that the population of the *s-cis* conformer will become greater in a polar solvent relative to the nonpolar solvent. Thus, it may be possible to assign some bands to the respective conformations.

The infrared spectra of *t*-butyl formate and 1,1-diethylpropyl formate were thus measured in carbon disulfide (2.64),*[2] acetone (20.7), acetonitrile (37.5), and *N,N*-dimethylformamide (DMF) (37.7). The results are shown in Fig. 5.

Apparently, the intensities of all the absorptions change. The outstanding feature of the change is

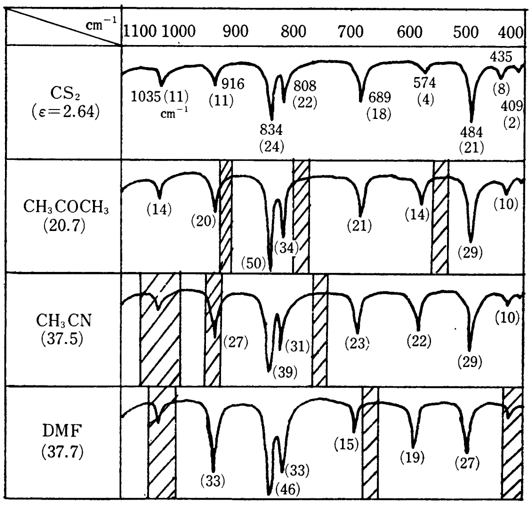


Fig. 5. Solvent effect of IR spectra of *t*-butyl formate.
The figures in parentheses are molar absorption coefficients.
The shaded range is a part of strong absorption of solvent itself.

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[18] In this skeletal deformation region, the assignment and calculation of each absorption of the ester were made only with methyl formate, methyl acetate, ethyl acetate, and methyl propionate. S. Ichikawa, Tokyo University, private communication.

*[2] The numbers shown in parentheses are dielectric constants.

that the intensities of the absorptions at 916 and 574 cm^{-1} become larger in comparison with the band at 689 cm^{-1}, as the solvent polarity increases.*[3] The results mean that the bands at 916 and 574 cm^{-1} can be assigned to some modes of vibration of the *s-cis* conformer. Since, as has been mentioned before, the intensities of these bands decrease on lowering of the temperature, it may now be said that the *s-cis* conformer of *t*-butyl formate is less stable than the *s-trans*. The solvent effect on the spectra of the 1,1-diethylpropyl formate is large, as is on *t*-butyl formate. This fact may be considered as a reflection of the presence of *s-cis* and *s-trans* isomers, since the population of the rotational isomers about the C–C axis of the ethyl groups is not affected to a great extent by the solvent polarity change; the dipole moment should not be affected too much by rotation about the bond in question.

Solvent Effect in the Region of the Carbonyl Stretching Vibration. The solvent effect on the far-infrared spectra of formates, as has been described above, naturally led the present authors to reinvestigate the carbonyl stretching region by means of the polar solvents. The results are given in Fig. 6.

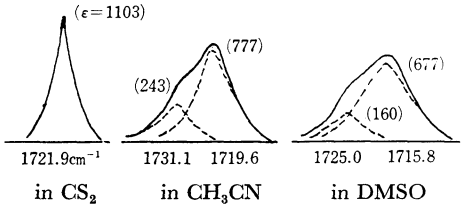
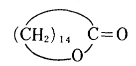


Fig. 6. Solvent effect on ν_{CO} of *t*-butyl formate.

It is apparent that *t*-butyl formate has at least two peaks in acetonitrile and dimethyl sulfoxide (DMSO) and that graphical seperation of these bands gives two peaks, the molecular extinction coefficients of which and the wave numbers of the absorption maxima of which, are also shown in Fig. 6. There are two possible reasons for the fact that *t*-butyl formate gives two absorption maxima in the polar solvents, whereas it gives only one peak in carbon disulfide. The first is the possibility that, although there is only one conformation, there are at least two species of solvation, the lower band representing the molecular species which are strongly solvated by the polar solvent. In this case, the exchange among these species is slow enough for resolution by infrared light. The second is the possibility that *s-cis* and *s-trans* conformers now give resolvable two bands. If the first possibility were really the case, however, other esters which exist in

TABLE 3. SOLVENT EFFECT ON ν_{CO} OF ESTERS
($c \approx 0.05$ mol/*l* at 20°C)

Solvent / Compound	CS_2 (2.64)*		CH_3CN (37.5)*		DMSO (48.9)*	
HCO_2Me	1733.2 cm^{-1}	(1150)**	1727.0 cm^{-1}	(1102)**	1719.0 cm^{-1}	(1111)**
HCO_2Et	1729.0	(1146)	1721.9	(1164)	1715.2	(1430)
HCO_2CHMe_2	1725.4	(1018)	1718.9	(901)	1716.6	(637)
HCO_2CMe_3	1721.9	(1103)	1719.6 1731.1	(777) (243)	1715.8 1725.0	(677) (160)
HCO_2CMe_2Et	1724.4	(1471)	1717.6 1731.0	(911) (281)	1714 1730	(851) (104)
HCO_2CMeEt_2	1723.1	(1356)	1716.8 1728.0	(820) (305)	1712 1725	(686) (104)
HCO_2CEt_3	1722.6	(1095)	1716.7 1727.7	(867) (219)	1715.6 1726	(730) (70)
$HCO_2C_{10}H_{17}$	1728.2	(1133)	1720.1 1724.2	(746) (244)		
HCO_2CPh_3	1740.8 1746.5	(684) (262)	1736 broad	(568)		
HCO_2Ph	1775.1	(—)	1762.2	(—)		
$HCO_2C_6H_3Me_2$-2,6	1769 1771	(—)*** (—)	1757 1768	(—)*** (—)		
$CH_3CO_2C_6H_3Me_2$-2,6	1763.2	(1127)	1759.1	(724)		
	1734.6	(772)	1727.6	(557)		

* Numericals shown in parentheses are dielectric constants at 20°C.
** Numericals shown in parentheses are molar absorption coefficients.
*** The molar absorption coefficients of the lower absorption of this compound are stronger than that of the higher in these two solvents.

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*[3] The wave numbers referred to are those observed in carbon disulfide.

one conformation should also give two bands in these polar solvents. Thus, the C=O stretching absorptions of various esters were determined and the results are shown in Table 3. It can immediately be pointed out that methyl formate, ethyl formate (whose conformations has been established to be *s-trans* by microwave spectroscopy),[7] and isopropyl formate have only one sharp symmetrical absorption in carbon disulfide, acetonitrile, and DMSO. The first possibility is, thus, not very likely. Therefore, the second becomes likely, since the existence of conformers has been proved for *t*-butyl formate from the far-infrared spectra (see below).

The reason why this compound gives only one band for C=O stretching in carbon disulfide may be that the wave number difference between the two conformers is so small that it cannot be resolved by the present optical instrument. As for the assignment of the two bands, the band at the higher wave number seems to correspond to the *s-cis* isomer. The reason for this assignment is two-fold. The first comes from a consideration of the population. The temperature dependence study has established that the *s-cis* isomer is the less stable one. Therefore, the weak band will correspond to less stable isomer. It may be argued that the absorption intensities per molecule for *s-cis* and *s-trans* are not known and that the reverse may be possible. However, consideration of bond dipole leads to the conclusion that, if the absorption intensity per molecule is different, it is the *s-cis* molecule which gives rise to a stronger absorption.[*4] The second reason for the assignment comes from the location of maximum absorption. From the same consideration as the intensity, it is natural to expect the *s-cis* conformer to give absorption due to C=O stretching at a higher frequency than the *s-trans*, since a higher energy will be necessary to excite the molecule when the two dipoles are arranged roughly parallel.

Table 3 shows that formate esters with bulky alkyl groups give two C=O stretching absorptions in polar solvents, whereas isopropyl formate gives only one absorption in any of the solvents investigated. These results indicate that the alkyl group in formate esters should at least be tertiary in order to make the existence of the *s-cis* conformer possible.

The aryl esters in Table 3 are worthy of special mention. Phenyl formate has only one absorption due to C=O stretching in both carbon disulfide and acetonitrile. It is expected to exist as the *s-trans* isomer. On the other hand, 2,6-dimethylphenyl formate shows two bands due to C=O stretching even in carbon disulfide. It is believed that the resolution is now possible between the *s-cis* and *s-trans* conformers in carbon disulfide. The same is true of triphenylmethyl formate. This assignment may be explained as follows: The conformation of phenyl formate (VII) must, at least, be nearly planar because of the resonance stabilization. However, the planar conformation is not possible for 2,6-dimethylphenyl formate (VIII) because of the steric effect of the methyl groups. If the models of the latter compound are written schematically, the *s-trans* and *s-cis* conformers may be represented as in Fig. 7. (VIIIa, VIIIb). In the *s-trans* conformation, those which cause the repulsion are the *p*-electron pair of oxygen and the π-electrons of the benzene ring. On the other hand, in the *s-cis* conformation, the interaction takes place between hydrogen of the formyl group and the π-electrons of the benzene ring. The latter interaction, which could even be rather attractive, is at least expected to be less repulsive because the van der Waals radius of hydrogen is far less than that of oxygen. Thus the *s-cis* conformer becomes less unstable than that

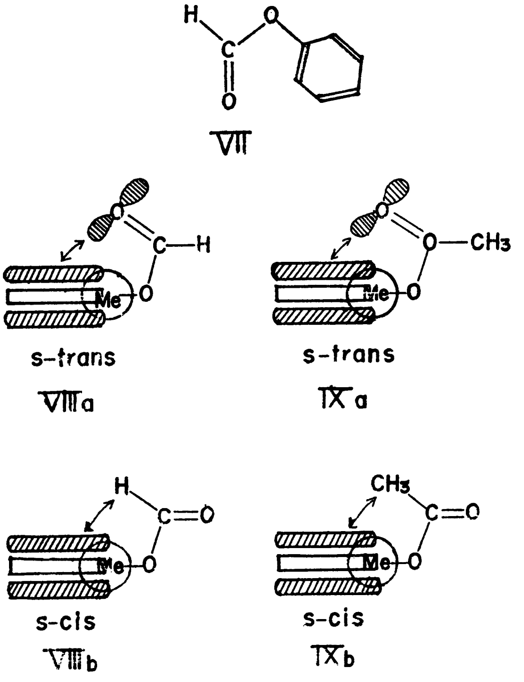
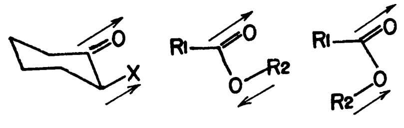


Fig. 7. Conformations of phenyl formate, 2,6-dimethylphenyl formate and 2,6-dimethylphenyl acetate.

[*4] It is well known that α-halocyclohexanone derivatives give stronger absorption due to C=O stretching per molecule when halogen is equatorial. This effect can be explained by considering the direction of the bond



VI *s-trans* *s-cis*

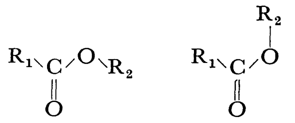
dipoles; the equatorial α-halocyclohexanone (VI) has dipoles as is shown above, which makes the change in dipole moment small on stretching the C=O bond. The situation is similar with the *s-cis* isomer of esters.

of the *s-trans*, although the interaction of the lone pair electrons of the two types of oxygen is still large in the *s-cis* conformation.

In this connection, the situation of 2,6-dimethylphenyl acetate (IX) is a different case. The repulsive interaction between the benzene ring and the methyl group of the acetyl seems to become large (Fig. 7, IXa and IXb), and this compound gives only one absorption due to C=O stretching in either carbon disulfide or acetonitrile.

Dipole Moment

It is known that the dipole moments of most esters are in the range from 1.4 to 2.0 D. Using the usual bond moments, the calculated values are 1.53 D and 3.40 D for the *s-trans* and *s-cis* isomers respectively. (The dipole moment of δ-valerolactone, which can take only the *s-cis* conformation, has been determined as 4.22 D[19]). Thus, the conformations of the ordinary esters are considered to be *s-trans*.

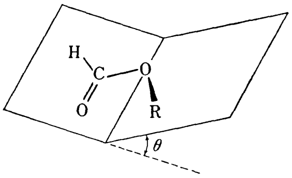


1.53 D 3.40 D

Calculated Dipole Moments.

In view of the above knowledge, it can be expected that the dipole moment data will provide another proof for the existence of the *s-cis* isomer. Krishna and his co-workers investigated along this line.[9] The results of the present work are tabulated in Table 4. Although the data are rather scattered, it may safely be said that methyl and ethyl formates and other acetates exist as *s-trans* conformers.

However, those of *t*-butyl formate, 1,1-diethylpropyl formate, and geranyl formate are a little too large to be attributed to the *s-trans* conformer only. Two reasons for the unusually high dipole moment may be considered. The first is the nonplanarity of the formate molecule ($\theta \neq 0$). Because of the steric requirement of the bulky alkyl group, the carbon atom attaching to the ether oxygen may not lie on the plane which is made by the formyloxy group. These conformations can be considered for both the *s-trans* and *s-cis* isomers. The second is the presence of both *s-trans* and *s-cis* conformers.



To clarify this point, the dipole moments of methyl formate, *t*-butyl formate, and 1,1-diethylpropyl formate were measured at various temperatures in benzene. The dipole moments of the compounds with bulky groups varied as the temperature changed, but that of methyl formate remained intact within the range of errors (Table 4). These results supported the idea that the second possibility is actually the case. The dipole moments of these compounds with bulky alkyl groups become large as the temperature becomes higher. This shows that the *s-cis* conformer is more unstable than the *s-trans* and agrees with the results obtained from the infrared spectra data.

Although it is now proved that the second possibility is actually the case, the first possibility cannot be ruled out. Indeed, the rather small excess of the dipole moment of *t*-butyl formate and 1,1-diethylpropyl formate over that of *s-trans* may reflect the nonplanarity of the molecule, since the nonplanar *s-cis* conformer may be expected to possess a smaller dipole moment as a result of the smaller contribution of the dipolar canonical structure. It is interesting to know in this connection that *t*-butyl acetate and ethyl acetate show larger dipole moments, in that order, than methyl acetate, whose structure has been shown by the microwave spectroscopic data to be planar.[7,8]

TABLE 4. DIPOLE MOMENTS OF ESTERS (in C_6H_6)

Compound	μ (D)	T°C	Compound	μ (D)	T°C
HCO_2CH_3	1.67	5	$HCO_2C(C_2H_5)_3$	2.23	15
	1.73	25		2.28	25
	1.73	35		2.29	35
$HCO_2C_2H_5$	1.96	25	*$HCO_2C_{10}H_{17}$[9]	2.57	25
$HCO_2C(CH_3)_3$	1.67	5	$CH_3CO_2CH_3$	1.45	25
	2.10	25	$CH_3CO_2C_2H_5$	1.88	25
	2.26	45	$CH_3CO_2C(CH_3)_3$[20,21]	1.91	25

* geranyl formate

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[19] R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

[20] C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, **53**, 527 (1931).

[21] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, (1955), pp. 303—309.

TABLE 5. n-π^* ABSORPTIONS OF CARBONYL OF FORMATES AND ACETATES
(in n-hexane or isooctane)

Compound	λ_{max} (mμ)	ε	Compound	μ_{max} (mμ)	ε
HCO_2CH_3	215.2	71	$CH_3CO_2CH_3$	209.8	57
$HCO_2C_2H_5$	215.7	82	$CH_3CO_2C_2H_5$	210.0	58
$HCO_2{}^nC_3H_7$	215.7	79*	$CH_3CO_2{}^nC_3H_7$	209.8*	56
$HCO_2{}^iC_3H_7$	215.9	75	$CH_3CO_2{}^iC_3H_7$	211.7	64
$HCO_2{}^nC_5H_{11}$	215.5	77*	$CH_3CO_2{}^nC_5H_{11}$	210.4*	63
HCO_2CMe_3	217.8	80	$CH_3CO_2CMe_3$	216.2	53
HCO_2CMe_2Et	218.5	72			
HCO_2CMeEt_2	223	116			
HCO_2CEt_3	226	155			
$HCO_2C_{18}H_{17}$**	238	163			

* Data from W. D. Closson and P. Haug[23]
** geranyl formate

Ultraviolet Absorption Spectra.

The ultraviolet absorption spectra of esters and lactones were measured by Closson and Orenski,[22] who pointed out that the n-π^* absorption of the carbonyl oxygen appeared at a longer wavelength with the *s-cis* conformation than with the *s-trans*. Therefore, the UV spectral technique will give another clue in the reseach for the *s-cis* conformer.

The ultraviolet absorption spectra of various esters have been determined; the results are shown in Table 5. It is apparent that those which have been proved by the other techniques to exist as conformational mixtures have absorptions at wavelength longer than 216 mμ. The absorption maximum is still shifted bathochromically when the alkyl group becomes bulkier. The ultraviolet absorption may be used as supplementary evidence for the presence of the *s-cis* isomer in esters.

Nuclear Magnetic Resonance Spectra.

It is not possible to learn the population of the *s-cis* and *s-trans* conformers of the ester by means of infrared spectroscopy because of the nonidentical absorption intensity per molecule. Nor is it possible to do so by dipole moment measurements, because the absolute value for each isomer is not known. However, it is possible by means of NMR spectroscopy, provided the exchange of the isomers is sufficiently slow on the NMR time scale. Thus, it seemed that it would be interesting to measure the NMR spectra of several formates at various temperatures. Methyl, ether, isopropyl, and *t*-butyl formates show sharp singlets at 7.97, 7.87, 7.88, and 7.83 ppm respectively in carbon tetrachloride at room temperature. Although it might be hoped that the signal might be resolved into two singlets in a solvent which would give a specific solvent effect, *t*-butyl formate shows a sharp singlet at 7.68 ppm from tetramethylsilane (TMS) in benzene. Thus, it is necessary to lower the temperature in order to slow down the rate of exchange. DMF has been chosen as a solvent for this study because it has a rather low melting point (−61°C) and its proton signal may be used as a control. The concentration of this solution was *ca.* 50% to avoid freezing during the measurement at about −100°C. *t*-Butyl formate in DMF has a singlet peak at 8.04 ppm from TMS at 20°C. whereas the peak broadens at −64°C. The signals are resolved into two at −94°C, the chemical shifts beeing 8.88 and 8.03 ppm from TMS. The chemical shifts do not change at −99°C. The area under the peak at 8.88 ppm corresponds to 14% of the total signals of formyl proton. The peak at 8.88 ppm is assigned to the *s-cis* isomer, and that at 8.03 ppm, to the *s-trans* isomer, because it is established by the infrared study that the *s-cis* isomer is less stable.[*5]

The rough thermodynamic parameters for the *s-cis* and *s-trans* isomers are shown in Table 6; they

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[22] W. D. Closson and P. J. Orenski, *J. Org. Chem.*, **32**, 3160 (1967).

[23] W. D. Closson and P. Haug, *J. Amer. Chem. Soc.*, **86**, 2384 (1964).

[*5] It may be argued that *t*-butyl formate and *N,N*-dimethylformamide (DMF) may form a complex and that there is an equilibrium between the complex and the monomer of the ester. In this case, the exchange between these species is slow enough to be detected on the NMR time scale at these low temperatures. In order to clarify this point, the NMR spectra of methyl formate were measured in DMF at a *ca.* 50% concentration at temperatures between 30°C and −95°C. The peak heights of formyl protons of methyl formate and DMF remained unchanged, although the chemical shift of the formyl proton of methyl formate shifted a little to a lower field (from 8.03 ppm to 8.06 ppm from TMS) as the temperature was lowered. These results support the idea that the splitting of the signal of *t*-butyl formate is due to the presence of rotational isomers and not to the presence of a complex molecule.

Table 6. The thermodynamic parameters for the *s-cis* and *s-trans* isomer equilibration of *t*-butyl formate

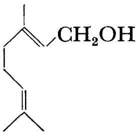
ΔH	-2.2 ± 0.7 kcal/mol
ΔS	$-9\ \ \pm2$ e.u.

are obtained from the equilibrium constants at −94°C and −99°C. It is impossible at the present to obtain the kinetic parameters for the rotation about the $\text{C–O}_{\text{ether}}$ axis of *t*-butyl formate, for the intensities of the two peaks are not the same and, moreover, vary according to the temperature. However, judging from the large chemical shift, $\Delta\nu=$ 0.85 ppm (*cf*, the fact that *t*-butyl formamide has a $\Delta\nu$ value of 0.23 ppm and shows two peaks at room temperature[4]), it is apparent that the activation energy for the rotation of *t*-butyl formate is smaller than that of the corresponding amide.

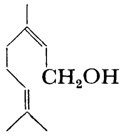
Conclusion

It has been established, by various spectroscopic techniques and by dipole moment measurements, that *t*-butyl formate exists as a mixture of the *s-cis* and the *s-trans* conformers. The other formate, which has a rather bulky group, shows also the presence of two isomers. These may be attributed to the steric effect of the alkyl group, which interfers severely with carbonyl oxygen; the steric repulsion is relieved when the *s-cis* conformation is taken, because the hydrogen of the formyl group is less bulky than the carbonyl oxygen.

A rather striking example is geranyl formate. Every piece of evidence studied so far has indicated the presence of the *s-cis* isomer in this compound. Geranyl is the primary alkyl group, and we cannot expect a great steric bulkiness. A further surprising fact is that neryl formate, an isomer of geranyl formate, shows no evidence of the presence of the *s-cis* isomer. These puzzling facts must be studied further.



Geraniol



Nerol

The authors wish to express their hearty thanks to Professor T. Shimozawa of Saitama University for the measurement of the dipole moments and to Dr. Y. Kawazoe of the National Cancer Center Reseach Institute for the NMR measurements. The authors are also indebted to Mrs. S. Ichikawa and Dr. Y. Koyama for their help in measurement of the far-infrared spectra and for their helpful discussions.