Conformations of the Esters. V.[1] The Conformations of Carbonates

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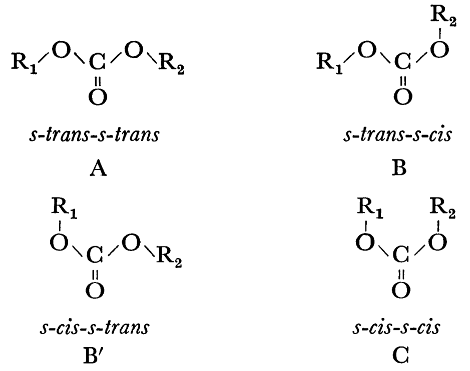
In alkyl or aryl carbonates, the presence of conformational isomers (*s-cis* and *s-trans*) has been confirmed by infrared and nuclear magnetic resonance spectroscopic techniques. The dipole-moment measurements also support the conclusions obtained from the spectroscopic data.

The conformation of the carbonate has been claimed by Kubo,[2] Thomson,[3] and Longster[4] to be *s-trans-s-trans* on the basis of the data on the dipole moments of dimethyl and diethyl carbonates. In the light of the fact that the *s-cis* conformer can exist together with the *s-trans* in some esters of formic acid which carry the bulky alkyl group,[5] and that carbamates have *s-cis* and *s-trans* conformers,[1] it seemed that it would be interesting to reinvestigate the conformation of carbonates, which are the analogs of esters.



s-trans-s-trans A

s-trans-s-cis B

s-cis-s-trans B′

s-cis-s-cis C

Fig. 1. Four conformational isomers of the carbonate.

In discussing the conformations of carbonates, the four conformers shown in Fig. 1 must be taken into account. C conformer (*s-cis-s-cis*) can be considered to be unimportant, for the repulsion between R_1 and R_2 groups is very large, even if both R_1 and R_2 groups are methyl groups. If the R_2 group is bulkier than the R_1 group ($R_2 > R_1$), the B conformer will be more stable than the B′ conformer, because the length of the $C–O_{ether}$ bond (1.36 Å) is longer than that of C=O (1.20 Å); hence, the repulsion between O_{ether} and R_2 in the B conformer can be expected to be smaller than that between C=O and R_2 in the B′ conformer. As to the chief factors governing the preference of the conformations of the ester, three factors (dipole-dipole interaction, lone pair-lone pair interaction, and the steric repulsion between the carbonyl and the alkyl groups or between the two alkyl groups) were described in an earlier paper.[5] In the carbonates, two additional factors must be taken into account in discussing the conformations: the dipole-dipole interaction between C–O and O–R_2 and the lone pair-lone pair repulsion between two ether oxygens(the so-called "rabbit ear effect",[1,6] (Fig. 2)[7]). With regard to the first factor, the B conformer is favored over the A conformation, in the nonpolar media, while with regard to the second factor, the A conformer is destabilized by the larger repulsion between the two ether oxygens. Therefore, the possibility of the existence of the *s-cis* conformer is larger in the carbonate than in the ordinary ester. The purpose of this paper is to present various sepectroscopic and dipole-moment data to confirm the existence of the *s-trans-s-cis* conformer in some carbonates.

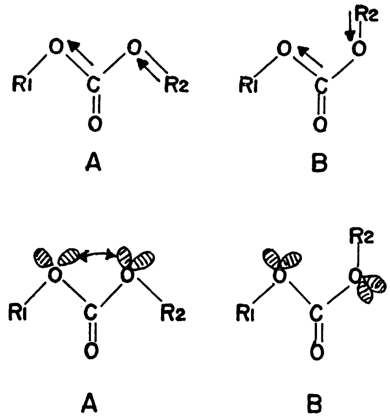


Fig. 2. Additional factors governing the conformations of the carbonate.

Experimental

The dimethyl and diethyl carbonates were of commercial origin and were purified by distillation before measurement. The ethyl methyl carbonate, *t*-butyl methyl carbonate, and 1,1-diethylporpyl methyl carbonate were prepared by pouring the corresponding sodium alkoxide into methyl chloroformate in dry ether with ice-cooling and then distilling under re-

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[1] Part IV: M. Ōki and H. Nakanishi, This Bulletin, **44**, 3148 (1971).

[2] a) M. Kubo, *Sci. Papers. Inst. Phys. Chem. Research., (Tokyo)*, **30**, 169 (1936). b) M. Kubo, Y. Morino, and S. Mizushima, *ibid.*, **32**, 129 (1937).

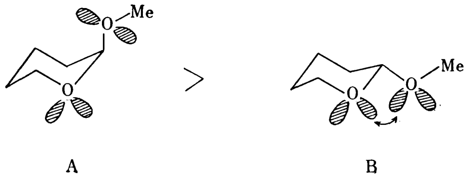
[3] G. Thomson, *J. Chem. Soc.*, **1939**, 1118.

[4] G. F. Longster and E. E. Walker, *Trans. Faraday Soc.*, **49**, 228 (1953).

[5] M. Ōki and H. Nakanishi, This Bulletin, **43**, 2558 (1970).

[6] a) R. O. Hutchins, L. O. Kopp, and E. L. Eliel, *J. Amer. Chem. Soc.*, **90**, 7174 (1968). b) E. L. Eliel, *Kemisk. Tedskrift*, **1969**, No. 6—7, 22. c) E.L. Eliel, *Accounts. Chem. Res.*, **3**, 1 (1970).

[7] In a heterocyclic system such as is shown below, Eliel called this lone pair-lone pair interaction the "rabbit ear effect." The A conformation, with an axial methoxy group, is more stable than the B conformation, with an equatorial methoxy group.



duced pressure. The diisopropyl carbonate, diphenyl carbonate, and bis(2,6-dimethylphenyl) carbonate were prepared from the corresponding alkoxide or phenoxide and phosgene. The methyl phenyl carbonate, 2,6-dimethylphenyl methyl carbonate, methyl 4-nitrophenyl carbonate, and 4-methoxyphenyl methyl carbonate were prepared by pouring methyl chloroformate into a mixture of the corresponding phenol and aqueous sodium hydroxide with ice-cooling.

$MeOCO_2$*t*-*Bu*: bp 52—53°C/57mmHg. NMR. (from TMS in benzene) 6.54 (3H, s), 8.63 (9H, s).

$MeOCO_2CEt_3$: bp 104—105°C/57 mmHg. NMR. 6.33 (3H,s), 8.20 (6H,q), 9.17 (9H,t).

i-$PrOCO_2$*i*-Pr: bp 139—140°C/760 mmHg. NMR.5.13 (2H, mul.) 8.88 (12H, d).

$MeOCO_2C_6H_5$: bp 112°C/23 mmHg. NMR. 2.75 (5H, m), 6.25 (3H, s) (in CCl_4).

$MeOCO_2C_6H_3Me_2$-2,6: bp 135°C/38 mmHg. NMR. 2.92 (3H, s), 6.15 (3H, s), 7.82 (6H, s) (in CCl_4). Found: C, 66.55; H, 6.76%; Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%.

$MeOCO_2C_6H_4NO_2$-4: mp 123°C NMR. 6.07 (3H, s).

$MeOCO_2C_6H_4OMe$-4: bp 110—112°C/2 mmHg. Found; C, 59.05; H, 5.24%; Calcd for $C_9H_{10}O_4$: C, 59.34; H, 5.53%.

$C_6H_5OCO_2C_6H_5$: bp 167—168°C/15 mmHg. NMR. 2.75 (10H, m) (in CCl_4).

The purities of the compounds used in this study were checked by studying their infrared spectra and NMR spectra, and by gas chromatography. The infrared spectra were measured on a Perkin Elmer single-beam grating spectrometer and a Hitachi EPI-G2 grating spectrophotometer. The NMR spectra were measured on JNM C-60, JNM-4H-100, and Hitachi R-20B Spectrometers. The dipole moment was measured by the heterodyne beat method, (the inaccuracy was about 0.05D at 1.0D). The calculation of the stability of dimethyl carbonate was carried out by the CNDO/2[8] method, using programs provided by the Computation Center of this University.

Results and Discussion

Nuclear Magnetic Resonance Spectra. In the expectation of obtaining some signs of the existence of A and B conformers, the NMR spectra of *t*-butyl methyl carbonate and 2,6-dimethylphenyl methyl carbonate were measured at room temperature. These two compounds were selected as the samples because they have a bulky alkyl or aryl group and because the repulsion between C=O and the R group is so large that the possibility of the existence of the *s-cis* conformer is also large. The results were, however, that both gave sharp singlets for the methoxy groups and did not give any sign of the existence of the two isomers. These results could arise for two reasons: the existence of a single isomer, or rapid exchange between isomers. If the latter is the case, there is a possibility that the singals split at lower temperatures. Thus, the NMR spectra of these compounds were measured at low temperatures in a CS_2–CH_2Cl_2 solvent, with toluene as the internal standard.

TABLE 1. THE CHANGE IN INTENSITY OF NMR PEAKS OF *t*-BUTYL METHYL CARBONATE

$MeOCO_2$*t*-Bu in $CS_2+CH_2Cl_2+C_6H_5CH_3$

	T°C				Chemical shift
	34	−70	−90	−120	τ
	1.37	1.31	1.15	1.27	2.86
C_6H_5-$\underline{CH}_3$	1.00	1.00	1.00	1.00	7.68
$O\underline{CH}_3$	1.29	1.11	0.95	0.84	6.41
$C(C\underline{H}_3)_3$	3.66	2.53	1.85	1.29	8.41

TABLE 2. THE INTENSITY CHANGE OF NMR PEAKS OF 2,6-DIMETHYLPHENYL METHYL CARBONATE

$MeOCO_2C_6H_3Me_2$-2,6 in $CS_2+CH_2Cl_2$

	T°C				Chemical shift
	34	−70	−90	−100	τ
arom-$\underline{H}$	1.00	1.00	1.00	1.00	2.87
$O\underline{CH}_3$	1.57	1.34	1.06	0.96	6.04
aom-$\underline{CH}_3$	2.22	2.22	1.92	2.07	7.31

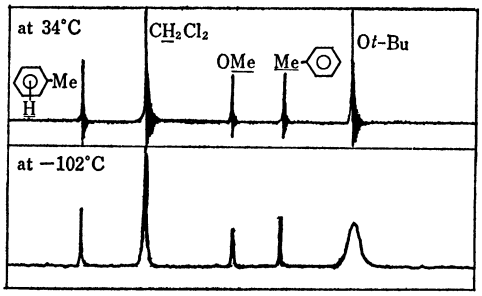
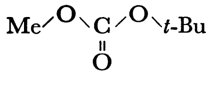


Fig 3. NMR spectra of $MeOCO_2$*t*-Bu.

The results are shown in Tables 1 and 2 and in Fig. 3. Neither the methoxy nor *t*-butyl methyl peak separated, even at low temperatures, but the peak of the *t*-butyl protons became very broad at −102°C. (The height of the *t*-butyl peak at −102°C is one third of that at 34°C, while the peak height of the methoxy at −102°C is 65% of that at 34°C.) These results can best be interpreted by assuming the presence of two or three conformers in this compound and by assuming that the exchange rate between these conformers is slow enough for the time scale of NMR at this low temperature. Judging from the fact that the broadest peak in *t*-butyl methyl carbonate at low temperatures is not the methoxy peak but the *t*-butyl, it may be postulated that the *t*-butyl group is more mobile, and that the A and B conformations are significant, but not the B′ conformation, because the influence of the anisotropy of the carbonyl must be large in determining the chemical shifts of these protons; the difference in the chemical shifts of the methyl groups in A and B′ conformers is expected to be at least as large as that of *t*-butyl protons. It may be argued that the difference in the chemical shifts of the methoxy protons in the A and B′ conformers is so small that the peak height decreases only slightly. However, this possibility is seen to be rather unlikely when the average anisotropy effects of the car-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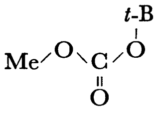
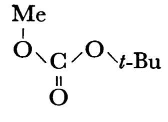

B


B′

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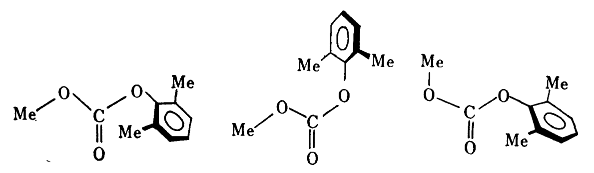
[8] a) J. A. Pople, D. P. Satry, and G. A. Segal, *J. Chem. Phys.*, **43**, S 129 (1965). b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S 136 (1965). c) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

bonyl group to methoxy and *t*-butyl protons are considered. Thus, the contribution of the B′ conformer is small, at least; this consideration conforms with that deduced from the steric effect.

In the case of 2,6-dimethylphenyl methyl carbonate, the situation is somewhat different. The broadest peak at low temperatures is not that of the aromatic methyl but that of the methoxy. These results may again be interpreted by assuming that the anisotropy effect of the carbonyl group is larger for the methoxy methyl than for the aromatic methyl, although there is some difference from the situation of the *t*-butyl methyl carbonate. Therefore, it can be assumed that the main *s-cis* conformation of 2,6-dimethylphenyl methyl carbonate is not B but B′ (Fig. 4). The population of the B conformer is considered not to be significant.



A B B′

Fig. 4. Conformations of 2,6-dimethylphenyl methyl carbonate.

Infrared Spectra of Carbonyl Stretching Vibration Absorption. The infrared spectra of carbonates have been measured by several authors,[9] and it has been reported that carbonates have only one carbonyl absorption.

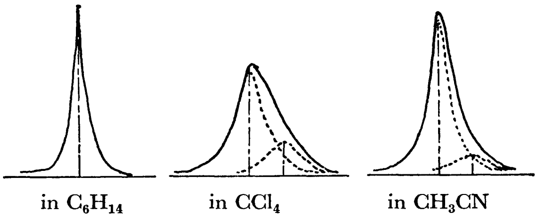


Fig. 5. ν_{CO} absorption of $MeOCO_2t$-Bu in three solvents.

No one has, however, reported about the shape of the carbonyl absorption. However, as has been described in previous papers,[1,5] some formates and carbamates have two carbonyl absorptions and can be assigned to two conformational isomers. From the NMR results on the carbonates, it is expected that a careful reinvestigation of the infrared spectra may produce further evidence for the conformational heterogeneity of the carbonates. Thus, the carbonyl stretching absorption was measured using an instrument with a high resolution. The results follow.

t-Butyl methyl carbonate was found to have an unsymmetrical carbonyl absorption in carbon tetrachloride and acetonitrile. This absorption was graphically separated into two absorptions using Lorenzian curves (Fig. 5). The infrared spectra of carbonyl absorptions of other carbonates were treated similiarly; the results are shown in Table 3.

Carbonates I, II, and III, whose two alkyl groups are relatively samll, all have one symmetrical carbonyl absorption in hexane, carbon tetrachloride, and ace-

TABLE 3. CARBONYL ABSORPTIONS OF THE CARBONATES

	Solvent / Compound	C_6H_{14} c=0.02 mol/l cm^{-1} (ε)	CCl_4 c=0.0004 mol/l cm^{-1} (ε)	CH_3CN c=0.02 mol/l cm^{-1} (ε)
I	$MeOCO_2Me$	1762.3 (1684)	1756.5 (988)	1755.8 (1400)
II	$EtOCO_2Et$	1752.1 (2089)	1746.3 (956)	1745.2 (1390)
III	$MeOCO_2Et$	1755.3 (1764)	1750.7 (915)	1749.8[a] (1409)
IV	$MeOCO_2t$-Bu	1750.7 (2089)	1739 (73)	1734 (80)
			1744 (891)	1744 (1339)
V	$MeOCO_2CEt_3$		1737 (55)	1734 (150)
			1744 (929)	1744 (1010)
VI	i-$PrOCO_2i$-Pr	1736 (90)	1731 (106)	1727 (52)
		1744 (2258)	1739 (790)	1738 (1403)
VII	$MeOCO_2C_6H_5$	1774 (1500)	1768 (682)	1767 (1131)
		1787 (109)	1779 (73)	1776 (54)
VIII	$MeOCO_2C_6H_3Me_2$-2,6	1771 (2489)	1765 (852)	1763 (1393)
		1783 (178)	1778 (58)	broad
IX	$MeOCO_2C_6H_4NO_2$-4		1774 (825)	1774 (986)
			1788 (67)	1784 (96)
X	$MeOCO_2C_6H_4OMe$-4		1766 (900)	1760 (167)
			1776 (68)	1766 (1952)
XI	$C_6H_5OCO_2C_6H_5$	1777 (187)	1759 (87)	1762 (m)
		1787 (2052)	1784 (845)	1784 (l)
		1799 (249)	1795 (22)	1794 (s)
XII	$(2,6\text{-}Me_2C_6H_3)_2CO_3$		1767 (114)	1762 (50)
			1777 (793)	1773 (1225)

a) Another weak peak exists at 1736 cm^{-1} (ε=66).

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[9] a) J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, **1957**, 618. b) B. M. Galehouse, S. E. Livingstone, and R. S. Nyholm, *ibid.*, **1958**, 3137. c) R. N. Nyquist and W. J. Patts, *Spectrochim. Acta*, **17**, 679 (1961). d) H. Minato, This Bulletin, **36**, 1020 (1963). e) K. V. Krishnamurty, G. M. Harris, and V. S. Sasti, *Chem. Rev.*, **70**, 171 (1970).

tonitrile solvents. However, compounds IV—XII, which have relatively bulky alkyl or aryl groups, show two carbonyl bands in these solvents (compound XI has three absorptions). These results may be interpreted in the following way. In compounds I, II, and III, the steric repulsion between C=O and R$_1$ or R$_2$ is small. Thus, these compounds take the conformation, A, which is the most stable. On the other hand, in compounds IV, V, and VI, which have a large alkyl group, the steric repulsion described above becomes serious and the A conformer is so destabilized that the B conformer can exist to a significant extent. The coexistence of the A and B conformers explains the two carbonyl bands. In compound IV (MeOCO$_2$*t*-Bu), the intensity of the higher wave-number absorption is stronger than that of the lower one. The consideration of the directions of the bond dipoles of C=O and R$_2$–O[1,5] suggests that the *s-cis* conformer has a higher frequency band than the *s-trans*.[10] Therefore, in *t*-butyl methyl carbonate the B conformer (*s-trans-s-cis*) must be more stable than the A conformer (*s-trans-s-trans*). The solvent effect is found to be such that the intensity of the higher frequency band increases in polar solvents more than in nonpolar solvents. Since the calculated dipole moment of the B conformer (2.1D) is larger than that of the A conformer (0.1D), the results presented here necessarily mean that the B conformer is the one which is prefered in the polar solvents. The situation is somewhat different in compounds VII, VIII, IX, and X from that in compound IV. In these compounds, the intensity of the absorption of the lower wave number is stronger than that of the higher one. In assigning the two absorptions to two conformers in alkyl carbonates, the directions of the two bond dipoles can be considered to be the main factor, whereas in the aryl carbonates, the stability of the resonance canonical structures in addition to the directions of the bond dipoles must be taken into account. Although there are difficulties in assigning the absorptions because of the complexities arising from the steric and electronic effects, the authors would like to assign the tentatively as in the case of dialkyl carbonates. The band at the higher frequency is thus assigned to the *s-cis* conformer. Diphenyl carbonate has three absorptions in the region of carbonyl stretching. Three conformers may be considered: *s-cis-s-cis*, *s-cis-s-trans*, and *s-trans-s-trans*. The interaction between the two benzene rings in the *s-cis-s-cis* conformer will, however, be repulsive, and the repulsion is considered to be too large for the conformer to exist. Therefore, two conformations, *s-cis-s-trans* and *s-trans-s-trans*, will suffice in discussing the conformations of this compound. Thus, one of the bands in the carbonyl region must be attributed to the enhancement of an overtone or combination tone due to the Fermi resonance. Bis-(2,6-dimethylphenyl)carbonate shows two absorptions in which the higher band is stronger. If the analogy of dialkyl carbonate is still applicable, then it can be considered that the *s-cis-s-trans* conformer is to be favored over the *s-trans-s-trans*.

Surveying the stabilities of these conformers in dialkyl carbonates, alkyl aryl carbonates, and diaryl carbonates, we find that the *s-cis* conformer more stable in the first carbonates, and the *s-trans* conformer is favored in the second carbonates, while in the last the *s-cis* conformer is again more stable, if the above-mentioned assignments are accepted. The origin of these stabilities remains to be explored.

Table 4. Carbonyl overtone of the carbonates

Solvent / Compound		CCl$_4$ $c=0.007$ mol/l cm^{-1} (ε)
I	MeOCO$_2$Me	3467 (0.3)
		3492 (4.4)
II	EtOCO$_2$Et	3474 (3.2)
III	MeOCO$_2$Et	3467 (0.5)
		3485 (2.9)
IV	MeOCO$_2$*t*-Bu	3456 (0.7)
		3476 (5.6)
VIII	MeOCO$_2$C$_6$H$_3$Me$_2$-2,6	3510 (4.9)
		3527 (0.4)

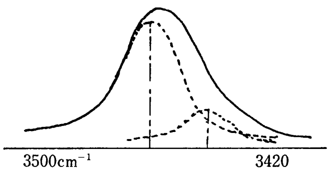

Fig. 6. Infrared spectra of carbonyl overtone of MeOCO$_2$*t*-Bu in CCl$_4$.

Infrared Spectra of Carbonyl Overtone. The infrared spectra in the carbonyl overtone region were measured in order to obtain further information about the conformations of the carbonates. The results are shown in Tabel 4 and Fig. 6. *t*-Butyl methyl carbonate (IV) has two absorptions of the carbonyl overtone, and the relative intensities of these two absorptions are almost the same as that of the carbonyl fundamental absorptions. These results suggest that the origin of the bifurcation of the carbonyl band is not the Fermi resonance but the heterogeneity of the conformations, thus supporting the assignment made earlier in this paper. The case of 2,6-dimethylphenyl methyl carbonate(VIII) is the same; the band at a lower frequency is stronger than that at a higher, as is observed in the carbonyl region. Dimethyl carobnate(I) and ethyl methyl carbonate(III), which show only one absorption in the carbonyl fundamental, give, astonishingly, two absorptions, and the intensity of the band at the higher wave number is stronger than that of the lower one, as in the case of *t*-butyl methyl carbonate. It is almost unbelievable that this bifurcation is due to Fermi resonance. Rather, this bifurcation may be explained by considering the existence of two conformers in these carbonates, although they are not detected by the C=O stretching absorption because of the small difference in frequencies. If this postulate is accepted, then in these carbonates with two small alkyl groups, the *s-cis* conformer can be considered from the relative intensity to be more stable than the *s-trans*.

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[10] This was suggested to be true by the results of the calculation of the bond order of the carbonyl of dimethyl carbonate by the CNDO/2 method.

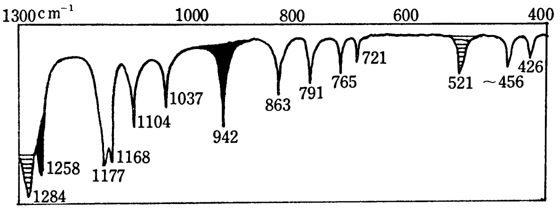
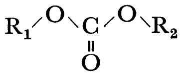


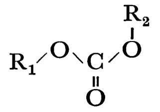
Fig. 7. Solvent effects on infrared spectra of $MeOCO_2t$-Bu in the region of 1300—400 cm^{-1}.
●: increasing band in polar solvent
◒: decreasing band in polar solvent.

Solvent Effect on the Absorptions in the Region of 1300—400 *cm*$^{-1}$. The B conformer of the carbonate should be more polar than the A conformer, judging from the arrangement of the bond dipoles. This implies that the population of the B conformer will increase in a polar solvent relative to in a nonpolar solvent. Thus, the infrared spectra of *t*-butyl methyl carbonate were measured in various solvents, such as carbon disulfide(2.64),[11] acetone(20.7), chloroform(4.81), *N*,*N*-dimethylformamide(37.7), and dimethyl sulfoxide(48.9), in the region of 1300—400 cm^{-1}. (Fig. 7) The intensities of the absorptions at 942 and 1258 cm^{-1} apparently increase in polar solvents, whereas the intensities of the absorptions at 521 and 1284 cm^{-1} decrease. This apparent solvent effect can be interpreted as implying that *t*-butyl methyl carbonate exist as a conformational mixture, each conformer having a different polarity.



0.1D

A



2.1D

B

Dipole Moment. The calculated dipole moment values are 0.1D for the A conformer and 2.1D for the B conformer.[12] The dipole-moment values obtained by CNDO/2 calculation are 0.27D for the A conformer, and 2.04D for the B conformer, of dimethyl carbonate. The results obtained with a benzene solution are given in Table 5. *t*-Butyl methyl carbonate (IV) has a little larger dipole moment than the other carbonates at room temperature, and the value at 49°C is smaller than that at 28°C. This temperature dependence of the dipole moment of this compound means that the conformers exist and that the more polar conformer, B or B′, is more stable than the less polar conformer, A. This is in accord with the results obtained from the infrared spectral study. Although it was made clear that the B or B′ conformer is more stable than the A conformer, the observed dipole moment of this compound is in between the two calculated values for the *s-trans* and *s-cis* conformers. The reason for these results may be considered to be an inaccuracy in the calculation of the dipole moments from the bond dipoles, but the twisting of the *t*-butyl group from the plane of the other part of the molecule can be another reason; the latter possibility is supported by the molecular model and by the results obtained with other esters in this laboratory, ($\theta \neq 0°$). The dipole moment values of compounds I, II, and III are in the range of 0.7—0.9D at room temperature, in between the two calculated values of the A and B conformers.[13] Since these values are colse to that of compound IV, it may be concluded that dialkyl carbonates take two comformations in the liquid phase. This conclusion is supported by the results of an infrared spectroscopic study in the overtone region of the carbonyl stretching, although there remains some ambiguity in the relative populations.

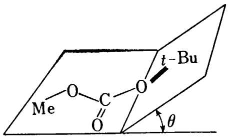


Table 5. Dipole moments of carbonates in benzene

	Compound	μ (D)	T°C
I	$MeOCO_2Me$	0.94	16
		0.91	28
II	$EtOCO_2Et$	0.90	25
III	$MeOCO_2Et$	0.71	28
IV	$MeOCO_2t$-Bu	1.00	28
		0.89	41
		0.80	49

Conclusions

Nuclear magnetic resonance and infrared spectroscopies and dipole-moment techniques have revealed that *t*-butyl methyl carbonate has the A (*s-trans-s-trans*) and B (*s-trans-s-cis*) conformers, the latter being more stable than the former, although the possibility of the existence of the B′ conformer (*s-cis-s-trans*) cannot be ruled out. This is in interesting contrast with the case of *t*-butyl formate, in which the *s-trans* conformer is more stable than the *s-cis*.[5] The difference may be explained by considering the stabilization of the B conformer of the carbonate due to the dipole-dipole interaction between C–O and R–O bonds and the destabilization of the A conformer due to the "rabbit ear effect." Other carbonates also give signs of conformational heterogeneity.

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11) The numbers shown in parentheses are dielectric constants.

12) The calculation was made on the basis of a bond moment value of 0.4D for the C–H bond, a 2.4D value for the C=O bond, and a 0.9D value for the C–O bond.

13) The dipole moments of dimethyl and diethyl carbonates in the gaseous phase were reported by Kubo *et al.*[2] not to change seriously from 55°C to 206°C. The carbonates are, therefore, considered to exist in a *s*-trans conformation only by these authors.