

Conformations of the Esters. IV. The Conformations of Carbamates

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It has been confirmed from an infrared spectral study of the C=O, N-H, and N-D stretching regions that primary, secondary, and tertiary carbamates take the *s-cis* and *s-trans* conformations with respect to the ester group. The nuclear magnetic resonance spectra and the results of dipole-moment studies support this conclusion.

The conformation of the ester has long been claimed to be *s-trans*, and the conformation of carbamates has been reported to be no exception (Fig. 1). Van der

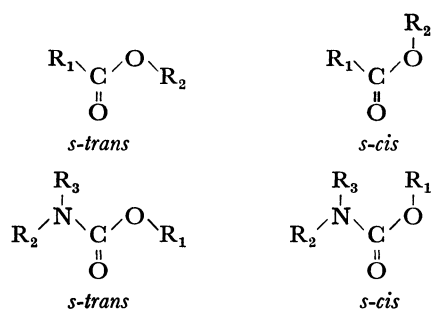


Fig. 1. The conformations of ester and carbamate.

Werf reported¹⁾ two conformations of the ester group in methyl *N*-methyl-*N*-alkylsulfonylcarbamates, but this conclusion has since been proved by NMR study to be not the case.²⁾ Since we have recently shown that the *s-cis* conformation can exist in some formates,³⁾ the search for the *s-cis* conformation in carbamates has been undertaken as an extension. The purpose of this paper is to present the results of such a study using infrared and nuclear magnetic resonance spectral techniques and dipole-moment measurements.

Experimental

Materials. The simple carbamates were prepared by the reaction of methyl chloroformate or ethyl chloroformate with aqueous or neat amine with cooling. Methyl *N*-phenylcarbamate was prepared by refluxing a mixture of aniline and methyl chloroformate in chloroform for an hour. Methyl *N*-deuterio-*N*-methylcarbamate (MeNDCO₂Me) was prepared by mixing methyl *N*-methylcarbamate with thirty molar deuterium oxide overnight at room temperature and by subsequent distilling under nitrogen. The physical constants of the compounds used in this study agree with those previously reported in the literature. The purity of the compounds was checked by studying their infrared and nuclear magnetic resonance spectra.

Apparatus. The infrared spectra were measured by using a Perkin Elmer 112G single-beam grating spectrometer (3600—3300 cm⁻¹, 2700—2400 cm⁻¹, 1800—1650 cm⁻¹) and a Hitachi EPI-G2 grating infrared spectrophotometer (4000—400 cm⁻¹). The nuclear magnetic resonance spectra were recorded on a JNM-4H-100 spectrometer. The dipole moment was obtained by the solution method, using benzene

as the solvent. The dielectric constant (ϵ) was measured by the heterodyne-beat method. The electronic polarizations (P_E) were computed from the table of bond refraction, and the atomic polarization (P_A) was taken as 5% of the electronic polarization. The values of the observed dipole moment include an inaccuracy of $\pm 0.02D$.

Results and Discussion

In discussing the conformations of carbamates, two conformers (*s-cis* and *s-trans*) may be considered when the nitrogen atom carries two identical substituents (Ia, Ib, IIIa, and IIIb in Fig. 2), whereas it is necessary to take four conformations into account when the nitrogen of the carbamate carries non-identical substituents, as is exemplified by the secondary amides, IIa, IIb, IIc, and IId, in Fig. 2.

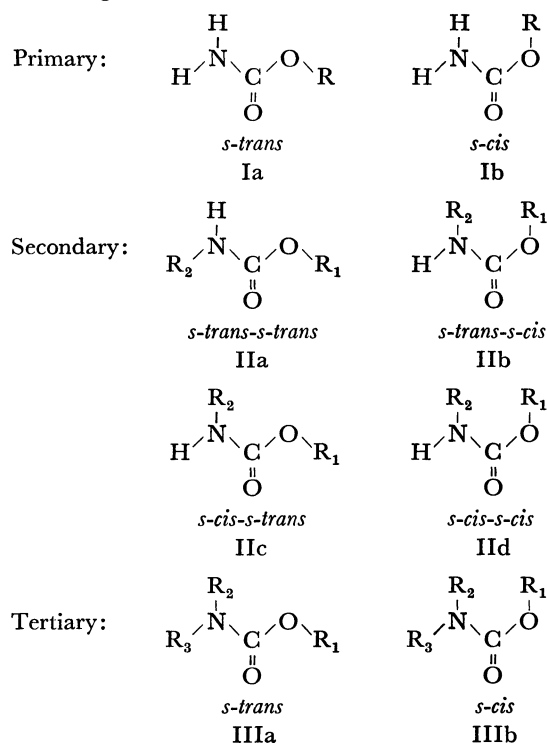


Fig. 2. The conformations of carbamate.

It is well known that the *s-trans* conformation is more stable than the *s-cis* in ordinary secondary amide. LaPlanche reported⁴⁾ that *N*-methylformamide (HCO-NHMe) has only an 8% *s-cis* conformer, and even *N*-*t*-butylformamide (HCONH-*t*-Bu) has only a 12% *s-cis* conformer, although in the latter compound the

1) S. van der Werf, T. Olinjma, and J. B. F. N. Engberts, *Tetrahedron Lett.*, **1967**, 689.

2) S. van der Werf and J. B. F. N. Engberts, *ibid.*, **1968**, 3311.

3) M. Ōki and H. Nakanishi, *This Bulletin*, **43**, 2558 (1970).

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

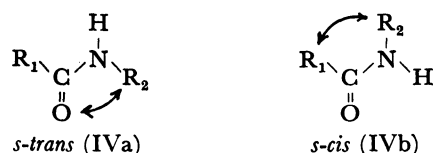
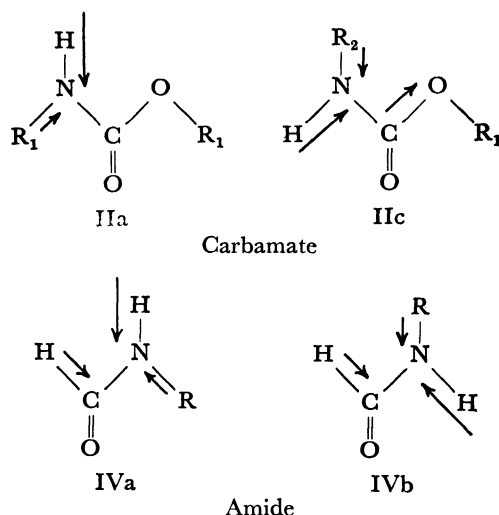


Fig. 3. The conformations of secondary amide.

R_1 is hydrogen, which is sterically small, and the steric repulsion between H and the *t*-butyl group in the *s-cis* conformer is considered to be smaller than that between C=O and the *t*-butyl group in the *s-trans* (Fig. 3) (thus, the *s-cis* conformer is expected to form the majority).

On the other hand, *N*-methyl acetamide (MeCONHMe) exists as the *s-trans* conformer only,⁵⁾ probably because the repulsion between two methyl groups in the *s-cis* conformer is too large for the *s-cis* conformer to exist. Comparing the situation of the carbamate with that of the amide, the alkoxy group in carbamate is larger than the hydrogen of the formyl group in formamide. Therefore, the repulsion between R_2 and OR_1 in IIc and IId (Fig. 2) must be larger than that between formyl hydrogen and R_2 in formamide (Fig. 3, IVb, $\text{R}=\text{H}$). The dipole-dipole interaction between H-N and the C- OR_1 bond is more favorable for IIa than that for IIc as far as the conformations of the amide part are concerned (see below). These considerations lead to the conclusion that the ratio of the population of the *s-trans* conformer with respect to the amide part of this carbamate (IIa and IIb) to that of the *s-cis* conformers (IIc and IId) is probably larger in carbamates than in ordinary amides. Therefore, it may be expected that the existence of the IIc and IId conformers at least can be neglected.



If both the *s-trans* and *s-cis* conformers of the amide group of carbamates should exist, two methyl peaks will appear in the NMR spectra of methyl *N*-methylcarbamate when the temperature of the measurement is lowered enough, because the rotation of the N-CO bond of the amide group has been reported to be slow

enough for the NMR time scale.^{6,7)} For example, methyl *N,N*-dimethylcarbamate ($\text{Me}_2\text{NCO}_2\text{Me}$) has been reported to have two *N*-methyl peaks in the NMR spectra at temperatures lower than -13°C .⁸⁾ On the other hand, methyl *N*-methylcarbamate (MeNHCO_2Me) shows only one *N*-methyl peak from 23°C to -100°C at 2.86 ppm from TMS in the $\text{CS}_2\text{-CH}_2\text{Cl}_2$ solvent at 100 MHz. This fact may be taken as suggesting that the exchange between conformers is not taking place on the NMR time scale. From the standpoint of steric considerations, it may be assumed that the IIa conformation is the most stable. Therefore, the IIa conformation is most probably the one which exists as a sole isomer. It may be argued that the chemical shift between *N*-methyls of IIa and IIb is too small to be resolved at present. However, from the above considerations, together with the discussion of the infrared spectral data to be given below, such a case can be considered rare.

TABLE I. CARBONYL ABSORPTIONS OF CARBAMATES

Compound		Solvent	
		CCl_4 $c=0.0002 \text{ mol/l}$	CH_3CN $c=0.005 \text{ mol/l}$
I	$\text{H}_2\text{NCO}_2\text{Me}$	1728 cm^{-1} (200) 1751 (1293)	1729 cm^{-1} (274) 1742 (614)
II	$\text{H}_2\text{NCO}_2\text{Et}$	1742.1 (657) broad	1725 (73) 1731 (649)
III	MeNHCO_2Me	1736 (777) 1748 (81)	1726.4 (861)
IV	EtNHCO_2Me	1725 (200) 1735 (1189)	1714 (104) 1724 (1100)
V	<i>i</i> -PrNHCO ₂ Me	1724 (200) 1732 (1885)	1712 (90) 1722 (803)
VI	<i>t</i> -BuNHCO ₂ Me	1721 (190) 1737 (1695)	1715 (62) 1726 (870)
VII	MeNHCO_2Et	1730 (638) 1740 (43)	1710 (73) 1721 (838)
VIII	PhNHCO_2Me	1734 (73) 1748 (1007)	1722 (41) 1735 (913)
IX	$\text{Me}_2\text{NCO}_2\text{Me}$	1711 (1333) 1720 (93)	1696 (99) 1705 (1147)
X	$\text{Et}_2\text{NCO}_2\text{Me}$	1696 (147) 1706 (1140)	1698 (1251)
XI	$\text{Me}_2\text{NCO}_2\text{Et}$	1706 (961)	1696 (970)

Infrared Spectra of Carbonyl-stretching Vibration. It is natural to anticipate that the *s-trans* and *s-cis* conformers of carbamates will have different carbonyl absorptions in their infrared spectra. Some authors have reported,⁹⁻¹²⁾ on the carbonyl absorption of carbamates, but no one has reported the observation of two carbonyl absorptions. Using a high-resolution infrared spectrophotometer, the carbonyl absorptions of

6) L. C. Breliere and J. M. Lehn, *Chem. Commun.*, **1965**, 426.7) B. J. Price, R. V. Smallman, and I. O. Sutherland, *ibid.*, **1966**, 319.8) E. Lustig, W. R. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967).9) S. Pinchas and D. Ben-Ishai, *J. Amer. Chem. Soc.*, **79**, 4099 (1957).10) A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, **1960**, 676.11) M. Sato, *J. Org. Chem.*, **26**, 770 (1961).12) R. A. Nyquist, *Spectrochim. Acta*, **19**, 509 (1963).5) a) S. Mizushima, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *J. Amer. Chem. Soc.*, **72**, 3490 (1950). b) I. Suzuki, *This Bulletin*, **35**, 540 (1962).

several methyl and ethyl carbamates were measured in carbon tetrachloride and acetonitrile. The results are shown in Table 1. It is apparent that almost all the primary (I, II), secondary (III—VIII), and tertiary (IX, X) carbamates have two carbonyl absorptions in both nonpolar and polar solvents. Since the concentrations of the measurement are dilute enough to exclude the solute association, this bifurcation of the absorptions can be said not to be due to the association effect. The intensity of the higher frequency absorption is stronger than that of the lower one in these two solvents with most compounds; compounds III, VII, and IX are exceptions. It is well known¹³⁾ that, in many cases of Fermi resonance, the intensities of bifurcated carbonyl absorption bands change dramatically when the polarity of the solvent is changed. In this case, however, the solvent effect is not so strong (except for III, VII, and IX). Therefore, Fermi resonance may not be the origin of the bifurcation of the carbonyl absorptions in the carbamates. Thus, it is most probable to assume that the existence of conformational isomers is the real origin of this bifurcation of carbonyl absorptions. As the calculated dipole moment values (as will be described later) of the *s-cis* conformer, IIb, are larger than those of the *s-trans* conformer, IIa, the population ratio of IIb to IIa can be expected to increase in polar solvents such as acetonitrile in comparison with in nonpolar carbon tetrachloride, as is the case of formates.²⁾ However, the solvent effect has been found to be very small in reality on the carbonyl absorptions of carbamates. The higher wave number band can be assigned to the *s-cis* conformer (Ib, IIb, and IIIb) and the lower one, to the *s-trans*, because the direction of the two dipoles of C=O and O—R is parallel in the *s-cis* conformer and is roughly antiparallel in the *s-trans* (Fig. 4); the latter necessitates less energy for stretching the carbonyl bond. Table 1 shows that the higher wave number band is stronger than the lower one in primary and secondary carbamates. This may be taken as evidence for the concept that, in these compounds, the *s-cis* conformer of carbamates with respect to the ester group is more stable than the *s-trans*.

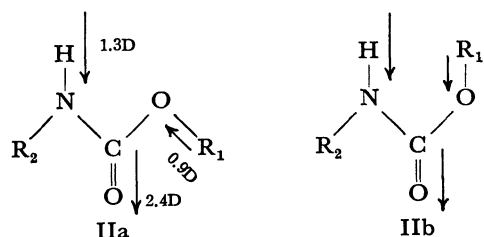


Fig. 4. The directions of the bond dipoles of carbamates.

Infrared Spectra of the N—H and N—D Stretching Vibrations and the First Overtone Band of the Carbonyl Absorption.

In order to obtain more information about the conformations of carbamates, the N—H stretching vibration absorptions in the infrared spectra were measured. The results are shown in Table 2. It is well known that

13) M. Ōki and H. Nakanishi, Part II. This Bulletin, **44**, 3144 (1971), and the references cited therein.

TABLE 2. ν_{NH} OF CARBAMATES

Compound	Solvent	
	CCl_4 $\epsilon=0.0003 \text{ mol/l}$	$2\nu_{\text{CO}}$
I $\text{H}_2\text{NCO}_2\text{Me}$	3433 cm^{-1} (30)	3456 cm^{-1}
	3444 (96)	3502
	3537 (33)	
	3558 (117)	
II $\text{H}_2\text{NCO}_2\text{Et}$	3432 (34)	3484
	3443 (130)	
	3542 (41)	
	3559 (129)	
III MeNHCO_2Me	3468 (24)	3472
	3476 (213)	3496
IV EtNHCO_2Me	3462 (219)	3451
		3471
V <i>i</i> -PrNHCO ₂ Me	3444 (18)	3448
	3452 (159)	3463
VI <i>t</i> -BuNHCO ₂ Me	3445 (17)	3442
	3451 (201)	3473
VII MeNHCO_2Et	3468 (21)	3460
	3476 (188)	3480
VIII PhNHCO_2Me	3438 (19)	3468
	3447 (249)	3496

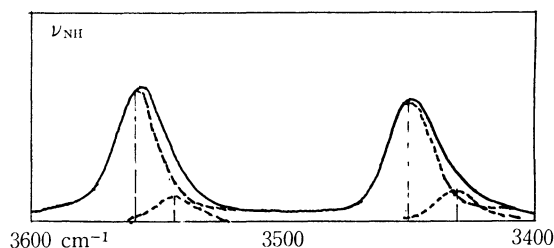


Fig. 5. Infrared spectra of ν_{NH} of methyl carbamate ($\text{H}_2\text{NCO}_2\text{Me}$).

the primary amide has two N—H stretching vibration absorptions, an antisymmetrical stretching mode at about 3550 cm^{-1} and a symmetrical one at about 3450 cm^{-1} . Compounds I and II have four bands; both antisymmetrical and symmetrical N—H stretching vibration bands are bifurcated. Secondary carbamates (III—VIII) have two N—H stretching vibration bands. In this region of 3600—3400 cm^{-1} , the first overtone of the carbonyl stretching vibration may appear. Therefore, the values of $2\nu_{\text{CO}}$ are listed in the last column of Table 2. Indeed, for example, the first overtone of the fundamental carbonyl absorptions of compound VIII appear at 3459 cm^{-1} ($\epsilon=4.2$) and 3487 cm^{-1} ($\epsilon=5.1$), but the intensity is much weaker than that of the fundamental tones. Generally speaking, the molecular extinction coefficient of the first overtone of carbonyl bands of carbamates is less than *ca.* 7. Since the intensities of the weaker bands in compounds I—VIII lie in the range of 41—17 (ϵ), the possibility of these weaker bands being the first overtones of carbonyl stretching absorptions is very small.

Further support for this assignment may be obtained by avoiding the influence of the overtone of carbonyl absorptions. Thus, the infrared spectra of the N—D stretching vibration were measured. Methyl *N*-deuterio-*N*-methylcarbamate (MeNDCO_2Me) shows also

two absorptions, at 2571 cm^{-1} ($\epsilon=16$) and 2578 cm^{-1} ($\epsilon=71$), at the low concentration of $c=0.0007\text{ mol/l}$ in carbon tetrachloride. This fact can most easily be explained assuming the existence of two conformational isomers.

In Table 2 the difference in the location between the higher and the lower N-H stretching absorptions in wave numbers is about 10 cm^{-1} . On the other hand, it has been reported¹⁴ that the difference in the N-H stretching vibration of the *s-trans* and *s-cis* conformers of amide is about $30\text{--}40\text{ cm}^{-1}$. Therefore, this small difference in the locations of the two absorptions may be taken as indicating that, in secondary carbamates, the conformers with respect to the amide group (IIc and IId) do not exist; this conclusion is in agreement with the NMR results. These small wave-number differences may be attributed to several factors, including the dipole-dipole interaction between H-N and $R_1\text{-O}$ bonds through a somewhat long distance (cf. Fig. 4). By analogy with the considerations used in the assignment of the carbonyl absorptions, the directions of the two dipoles (H-N, $R_1\text{-O}$) in the *s-cis* conformer (Ib or IIb) probably give rise to the absorption of the N-H stretching at the higher wave number; therefore, the lower one must be assigned to the *s-trans* conformer (Ia or IIa). The intensity of the higher band is stronger than the lower band (Table 2); from these N-H stretching band studies, also, it is confirmed that the *s-cis* conformer (Ib or IIb) is more stable than the *s-trans* conformer (Ia or IIa). The results of the infrared study of N-H and N-D stretching vibration absorptions apparently shows that compound III has two conformations and that the *s-cis* conformer is more stable than the *s-trans*. The abnormality of the carbonyl bands of this compound, that is, the fact that it gives a stronger absorption at lower wave number, may be attributed to the Fermi resonance. The same may also be said about compound VII.

As to the tertiary carbamates, IX, X, and XI, the carbonyl absorptions are complicated. The intensity ratio of the two bands is reversed in compounds IX and X, and compound XI has only one symmetrical band in these two solvents. In order to know more about the conformation of tertiary carbamates, the first overtone spectra of compounds IX and X were measured. Compound IX has only one peak, at 3407.1 cm^{-1} ($\epsilon=8.18$), and compound X has two peaks, at 3360 cm^{-1} ($\epsilon=0.23$) and at 3393 cm^{-1} ($\epsilon=3.42$), at the concentration of 0.013 mol/l in carbon tetrachloride. These results may mean that the Fermi resonance is one of the factors causing the complication of the spectra at the carbonyl region, but it is impossible to draw a solid conclusion without reservation at the present time.

Dipole Moment. The dipole-moment values of methyl *N,N*-dimethylcarbamate (IX) are found to be 2.55D at 16°C and 2.59D at 31°C in a benzene solution. The calculated dipole moment values are 1.38D for the *s-trans* with respect to the ester group and 3.48D for the *s-cis* (bond moment: C=O : 2.4D , C-H : 0.4D , C-N : 0.4D , C-O : 0.9D). This calculation was made assuming that these conformations are all on one plane, but the O-Me group may be considered to be out of the plane of the amide group because of the steric repulsion between *N*-methyl and *O*-methyl groups. Since the error is estimated to be $\pm 0.02\text{D}$, these results may be taken as indicating that the *s-cis* conformer is more stable than the *s-trans* conformer in this compound.

Nuclear Magnetic Resonance Spectra. To obtain information about the conformations of carbamates, the nuclear magnetic resonance spectra of methyl *N*-methylcarbamate (MeNHCO_2Me) were measured from 23°C to -100°C in the $\text{CS}_2\text{-CH}_2\text{Cl}_2$ solvent. Only at about -100°C the peak of the methoxy methyl group began to broaden, while the peak of the *N*-methyl group was almost unchanged throughout this temperature range. These phenomena may be taken as further evidence for the existence of the conformational equilibrium of the ester group in this carbamate.

From the infrared and nuclear magnetic resonance spectra and the dipole-moment study, it can be concluded that, in primary and secondary carbamates, two conformers with respect to the ester group exist and the *s-cis* conformer is more stable than the *s-trans*, and that the same may be true in tertiary carbamates. Judging from the steric effect, this fact is very surprising, particularly in connection with the tertiary carbamate, for in these compounds the steric repulsion between *N*-alkyl and *O*-alkyl groups is expected to be large. This phenomenon may be explained partially by two factors; the first is the stabilization of the *s-cis* conformation due to C-N and O- R_1 bond dipolar interaction, and the second is the destabilization of the *s-trans* conformation due to the repulsion between the lone-pair electrons of ether-oxygen and nitrogen (the so-called "Rabbit Ear"; cf. E. L. Eliel (Fig. 6)¹⁵ in heterocyclic compounds.).

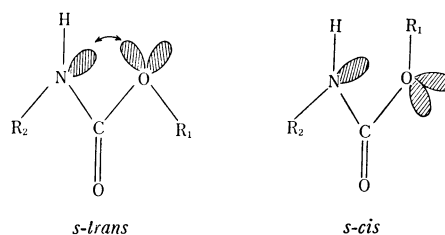


Fig. 6. "Rabbit Ear" effect in carbamate.

14) a) V. R. A. Russel and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956). b) R. L. Jones, *J. Mol. Spectry.*, **11**, 411 (1963).

15) a) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *J. Amer. Chem. Soc.*, **90**, 7174 (1968). b) E. L. Eliel, *Kemisk. Tidsskrift*, (1969), No. 6-7, 22.