THE CONFORMATION OF SOME TRIMETHYLSILYLESTERS BY SPECTROSCOPIC METHODS

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The doublet structure of $\nu(C{=}O)$ bands in the IR absorption spectra of some trimethylsilylesters of carboxylic acids XCOOY [$X = CCl_3, CCl_2H, CClH_2, C(CH_3)_3$; $Y = Si(CH_3)_3, CH_2Si.(CH_3)_3$] indicates conformational heterogeneity. The conformations of these esters were studied by analyzing the changes in IR spectra caused by solvent and temperature effects.

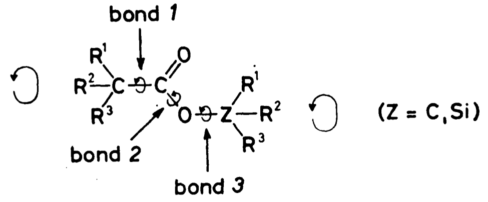
This report continues our work[1] on the role of the silicon atom in bonding and nonbonding interactions with a carbonyl group, as observed in IR spectra of trimethylsilylesters of carboxylic acids $RCOOSi(CH_3)_3$ (R = alkyl, halogenoalkyl, alkoxy, aryl and trimethylsilyl). The interpretation of IR spectra of these esters, which was presented in terms of rotational isomerism[1], is supported and enlarged in this paper by results obtained from the study of IR spectra of various model esters measured at different temperatures and in different solvents, and by ^{13}C NMR spectra measurements. The following molecules were treated: $Cl_2HCCOOCH_2Si.(CH_3)_3$ (*I*), $ClH_2CCOOCH_2Si(CH_3)_3$ (*II*), $(CH_3)_3CCOOCH_2Si(CH_3)_3$ (*III*), $Cl_2HCCOO(CH_2)_3CH_3$ (*IV*), $(CH_3)_3CCOOC(CH_3)_3$ (*V*), $Cl_3CCOOSi(CH_3)_3$ (*VI*), and $(CH_3)_3CCOOSi(CH_3)_3$ (*VII*).

EXPERIMENTAL

The preparation of the compounds studied and the method of IR spectra measuring were described in ref.[1]. The following solvents were used for the IR measurements: carbon tetrachloride, carbon disulfide, isopropanol, acetonitrile, and deuteriochloroform. Solute concentrations (in mole fraction) were 0·002—0·01. The temperature was varied from −85° to 30°C. The spectra were recorded on a Zeiss-Jena spectrophotometer Model 75 IR coupled on-line with a Robotron computer KSR 4100. The ^{13}C NMR spectra were measured on a Varian XL 200 instrument. The spectra of compound *II* were measured in the following solvents (and at temperatures): CD_3CN (23°C), $CDCl_3$ (23°C and −60°C), $CDBr_3$ (−60°C and −90°C) and CD_2Cl_2 (23°C and −90°C). The spectra of compound *I* were measured in CD_3CN at room temperature and in CD_2Cl_2 at 23°C and −90°C.

RESULTS AND DISCUSSION

In ester molecules under study, three centers of hindered internal rotation need to be considered: the C—C bond in the "acidic" part of the molecule (bond *1*), the C—O bond of alkoxy group (bond *2*), and the O—C bond from the "alcoholic" part (bond *3*). Theoretically, the rotations around all the three bonds should be assumed (see Scheme 1). In practice, however, hindered rotation around the C—O bond (bond *2*) may be disregarded. A relatively strong "lone pair effect" (a strong inter-



SCHEME 1

TABLE I
Solvent effect on $\tilde{\nu}$(C=O) (in cm^{-1}) in selected esters.

Compound	Solvent					
	CCl_4	CS_2	Toluene	Isopropanol	$CDCl_3$	CH_3CN
I^a	1 763 1 742	1 763 1 740		1 761 1 743	1 753 1 738	1 756^b 1 741^b
II	1 759 1 732	1 759 1 732	1 759 1 733	1 738^c	1 745 1 730	1 759^d 1 733^d
III	1 722 1 697	1 720 1 698	1 724 1 698	1 726 1 708	1 709	1 716
IV	1 766 1 744	1 764 1 744	1 763 1 743	1 763 1 747	1 756 1 740	1 757 1 743
V	1 721		1 721	1 724 1 699	1 712	1 714
VI	1 752		1 749	1 747^c	1 743	1 766 1 745
VII	1 712	1 705	1 710	1 710 1 692		1 704

^{a} 1 755 and 1 738 cm^{-1} in CD_2Cl_2; ^{b} 1 756 and 1 742 cm^{-1} in CD_3CN; ^{c} broad band; ^{d} 1 749 and 1 730 (shoulder) cm^{-1} in CD_3CN.

action between lone electron of the two oxygen atoms in the *s-trans* conformation of the ester group) causes that the O=C—O—C group exists predominantly in the *s-cis* form. It is every reason to believe that this concept of a structure known[2] from simple ester molecules may also be applied to more complicated cases such as to those studied in this work.

Let us first discuss the internal rotation around the C—C bond (bond *1*). The IR spectra of esters with $R^1 = R^2 \neq R^3$ (e.g. $R^1 = R^2 = H$, $R^3 = Cl$ or $R^1 = R^2 = Cl$, $R^3 = H$) show a doublet $\tilde{\nu}(C{=}O)$ band indicating the existence of two rotational isomers. In cases with $R^1 = R^2 = R^3$, when rotation around the C—C bond does not generate "unsymmetrical" nonequivalent structures, the single $\tilde{\nu}(C{=}O)$ band is consistent with existence of only one conformer, as it was found with compounds *IV*, *V* and *VII*. The results presented in Table I show also the wavenumber dependence of the $\tilde{\nu}(C{=}O)$ band on the inductive effect of substituents R^1, R^2 and R^3, as well as field effects between C—R and C=O bonds. Internal rotation around the O—C bond (bond *3*) leading to distinguishable conformers is seen in spectra of compound *III*; the doublet structure of the $\tilde{\nu}(C{=}O)$ band cannot be explained by internal rotations around the C—C bond (bond *1*) and C—O bond (bond *2*). Surprisingly, the wavenumber difference between the $\tilde{\nu}(C{=}O)$ band branches of the two conformers is approximately of the same value as that found in the spectra of conformers with rotation around bond *1*. Esters not exhibiting this type of internal rotation do not show splitting (see Table I, compounds *V*, *VI* and *VII*. With com-

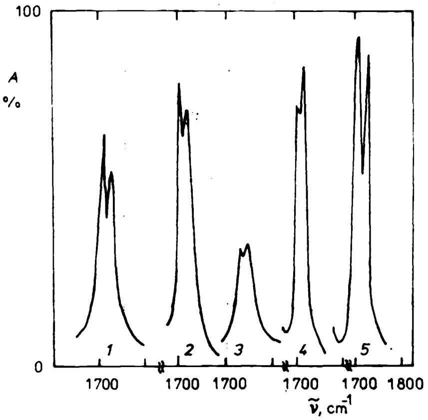


FIG. 1

Effect of solvents on $\tilde{\nu}(C{=}O)$ bands of $Cl_2HCCOOCH_2Si(CH_3)_3$: *1* carbon tetrachloride, *2* isopropanol, *3* deuteriochloroform, *4* acetonitrile, and *5* carbon disulfide

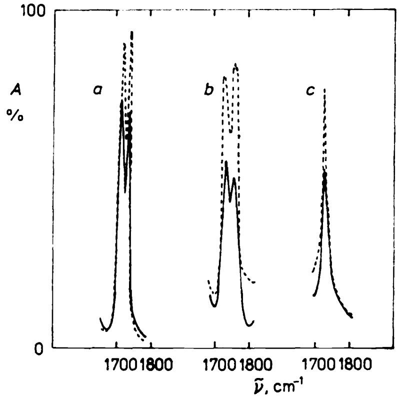


FIG. 2

The effect of temperature on $\tilde{\nu}(C{=}O)$ bands of *a* $Cl_2HCCOOCH_2Si(CH_3)_3$, *b* $ClCH_2.COOCH_2Si(CH_3)_3$, *c* $(CH_3)_3CCOOSi.(CH_3)_3$, measured in CS_2 at 30°C (full line) and −85°C (dashed line) pounds *I*, *II* and *IV* rotation around two centers may occur (bond *1* as well as bond *3*) and therefore four conformers may be expected. But four conformers are difficult to detect by IR spectroscopy.

The interpretation of IR spectra of the esters under discussion must anyway be done with caution. In some cases no splitting of the $\tilde{\nu}(C=O)$ band is observed in the IR spectra even if it is expected. The lack of evidence of this splitting comes from an uneven shift of one branch of the doublet caused by the polar solvents ($CDCl_3$, CH_3CN). This makes the doublet structure of $\tilde{\nu}(C=O)$ not resolvable under experimental conditions used. On the other hand, there is a splitting found in solutions of isopropanol, which cannot be explained by conformational heterogeneity. In this case the splitting is caused by the bifunctional behaviour of isopropanol as a solvent: the solute forms not only hydrogen bonded complex (with the OH group of isopropanol), but it also exists in a "free", nonbonded form. The $\tilde{\nu}(C=O)$ doublet in the IR spectra of compounds *V* and *VII* seems therefore to be formed by free and bonded carbonyls of a single conformation of the given ester. The doublet structure of the $\tilde{\nu}(C=O)$ band observed for compound *VI* in acetonitrile is not properly explained. The effect of solvent and temperature changes were used for the determination of structures of the individual conformers. From Fig. 1 it is seen that the intensity of the high wavenumber doublet branch increases on going from nonpolar to polar solvents. It is therefore evident that the high wavenumber branch belongs to a rotamer with the larger permanent electric dipole moment. Temperature changes show (e.g. in the case of compounds *I* and *II* shown in Fig. 2) that the conformers with a larger dipole moment are also thermodynamically more stable: the higher wavenumber branch increases in intensity as the temperature decreases.

The ^{13}C NMR spectra of mono and dichloro acetoxymethyl derivatives studied at various temperatures in some selected solvents showed all lines as narrow singlets with only one exception mentioned below. The conformational exchange is probably too fast to distinguish the rotamers by NMR spectroscopy. The exception was the spectrum of compound *II* in $CDBr_3$ at $-90°C$. Under these conditions, all carbon lines (except the $SiCH_3$ line) are split into doublets with intensities in the ratio of about 1 : 2. Since the splitting (0·9 Hz) was also observed in all solvent lines, we believe that it indicates formation of complexes between solute and solvent.

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