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**CONFORMATIONAL STRUCTURE AND VIBRATIONAL SPECTRA
OF METHYL ESTERS OF SIMPLE ALIPHATIC ACIDS**

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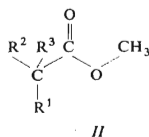
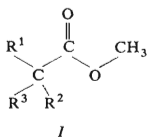
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For the elucidation of the conformational structure of some polymers carrying ester groups (*e.g.* of poly(methyl methacrylate) and poly(methyl acrylate)), it is important to know the orientation of ester groups with respect to the carbon chain. The conformation of the ester group with respect to the aliphatic acid residue was therefore studied by means of vibrational spectra of the simplest models, *i.e.* of methyl acetate, methyl propionate, methyl isobutyrate and methyl pivalate. Theoretically, the ester group can form both *cis* and *trans* isomers; as in the alkyl esters of aliphatic acids only the *cis* form has always been found¹⁻³, the *trans* form will not be considered in this study.

Infrared spectra in the range 400–3500 cm⁻¹ were measured on the Zeiss UR-10 spectrophotometer. The Raman spectra were measured on the spectrophotometer DFS-12, using a He-Ne laser (30 mW) as excitation source. The temperature dependences of infrared and Raman spectra were measured in special cells^{4,5}.

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The methyl esters of aliphatic acids can exist in these forms



Structure *I* has the carbonyl group in *syn* position with respect to one of the substituents R_1, R_2 ,

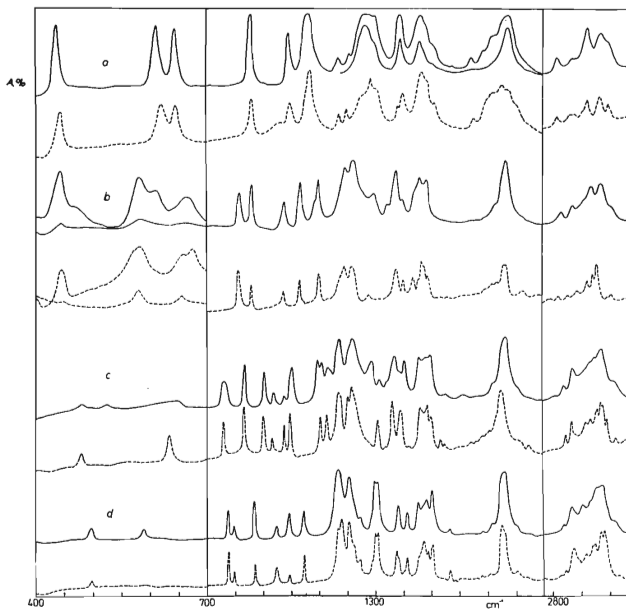


FIG. 1

Infrared Spectra of Methyl Acetate (*a*), Methyl Propionate (*b*), Methyl Isobutyrate (*c*) and Methyl Pivalate (*d*)

..... solid, — liquid.

or R_3 , and structure *II* has the $C=O$ group *trans* with respect to R_1 , R_2 or R_3 . From a comparison of infrared spectra of methyl acetate (Fig. 1a) and of methyl pivalate (Fig. 1d), measured both in liquid and in solid state, no "freezing out" of bands can be observed upon crystallization. It is thus evident that only one conformer is present in each of the two compounds. From the spectra it cannot be decided if this is the form *I* or *II*. Similar structures have been studied by Shimanouchi⁶ in aliphatic ketones; there it could be shown that the stable conformers contain the carbonyl group in *syn* position with respect to methyl(*syn* CO/CH_3) or to hydrogen (*syn* CO/H). In analogy to these results we assume that also in methyl acetate and in methyl pivalate, the stable forms contain the carbonyl group in *syn* position with respect to hydrogen or to a methyl group. In this conformation, oxygen bound by single bonds is in *trans* position with respect to the substituents R_1 , R_2 or R_3 . From conformational studies of esters it is known⁷ that oxygen preferentially forms an all-*trans* chain with the carbon atoms; this finding also confirms the energetic preference of conformers with carbonyls in *syn* position with respect to substituents.

If only the *cis* form of the ester group, and *syn* position of the carbonyl with respect to methyl or hydrogen on neighbouring carbon atom are considered, there still remain two possible conformers, *syn* CO/CH_3 and *syn* CO/H , in methyl propionate and methyl isobutyrate.

Upon transition from liquid to solid state, the bands at 487, 1075 and 1332 cm^{-1} disappear in the vibrational spectra of methyl propionate (Fig. 1c), and the bands at 520, 1087 and 1275 cm^{-1} disappear in the spectra of methyl isobutyrate; simultaneously, the width of the band at 760 cm^{-1} (which is a doublet in the liquid state) is reduced remarkably. This indicates that in the liquid state, these compounds contain both of the above mentioned possible conformers.

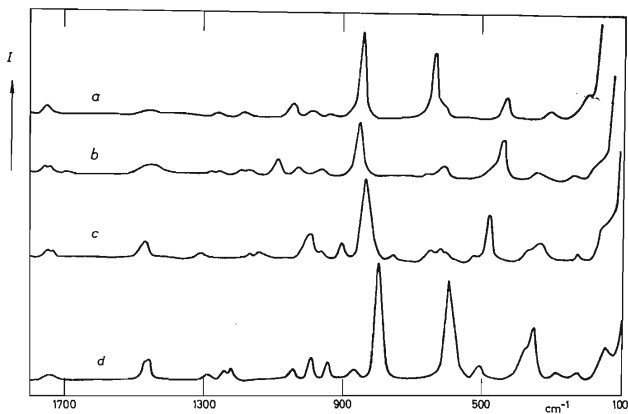


FIG. 2

Raman Spectra of Methyl Acetate (a), Methyl Propionate (b), Methyl Isobutyrate (c) and Methyl Pivalate (d) in Liquid State

TABLE I

Wavenumbers (cm^{-1}) and Depolarization Factors of C—C—O Bending Vibrations in Methyl Esters of Aliphatic Acids in the Liquid State.

Band intensities: very strong (vs), strong (s), medium (m), weak (w), very weak (vw), as. shoulder (sh).

Ester	Raman spectra		Infrared spectra	
	<i>syn</i> CO/CH ₃	<i>syn</i> CO/H	<i>syn</i> CO/CH ₃	<i>syn</i> CO/H
Acetate		436 s (0.5)		435 m
Propionate	487 vwsh	446 vs (0.5)	480 wsh	444 w
Isobutyrate	523 w (0.5)	481 s (0.4)	522 w	478 w
Pivalate	502 m (0.6)		497 w	

The infrared and Raman spectra of the studied compounds (Fig. 1, 2) contain several pairs of conformationally sensitive bands. The range of the C—C—O bending vibrations, 435 to 530 cm^{-1} (Table I), is especially suitable for the determination of conformers stable in the solid state. Methyl acetate, in which the only possible form is *syn* CO/H, and methyl pivalate, where the only form is *syn* CO/CH₃, exhibit in this range only one band each, at 436 and 502 cm^{-1} , respectively. On the other hand, in liquid state methyl propionate and methyl isobutyrate exhibit two bands each in this range; we assign the bands with higher wavenumbers to the form *syn* CO/CH₃, and the bands with lower wavenumbers to the form *syn* CO/H. As in the crystalline state only the bands at lower wavenumbers (447 cm^{-1} in methyl propionate and 481 cm^{-1} in methyl isobutyrate) are present, both these compounds are assumed to crystallize in the form *syn* CO/H (Table I). The correctness of this assignment can be checked by the intensities of these bands in infrared spectra. In methyl propionate, where the population of conformer *syn* CO/H is twice larger than that of conformer *syn* CO/CH₃, at room temperature the band at lower wavenumber is stronger, whereas in methyl isobutyrate where the population of the form *syn* CO/CH₃ is twice larger than that of *syn* CO/H, the intensities of both bands are approximately equal.

Similar intensity relations are found in infrared spectra of methyl propionate at 1087 and 1100 cm^{-1} , and in methyl isobutyrate at 1075 and 1090 cm^{-1} . In methyl isobutyrate the band at lower wavenumber, in methyl isobutyrate that with higher wavenumber is the more intense. In both cases, during crystallization the intensity of the band at higher wavenumber increases, and that of the band at lower wavenumber decreases.

From the temperature changes of intensities, the bands at higher wavenumbers can be assigned as characteristic of the conformer *syn* CO/H, confirming the assignment of the C—C—O bending vibrations.

From these results it may be concluded that in compounds carrying an ester group, the forms with the carbonyl in *syn* position with respect to hydrogen will be more stable than the forms with carbonyl in *syn* position with respect to methylene or methyl groups of the parent aliphatic acid.

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ANIONIC POLYMERIZATION OF 2-METHOXYETHYL METHACRYLATE AND 2-(DIMETHYLAMINO)ETHYL METHACRYLATE

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It follows from a series of papers dealing with the polymerization of methyl methacrylate initiated with the alkali metals compounds, that the stereospecificity of polymers prepared in the same solvents depends on the alkali metal used^{1,2}. Identical results were found during polymerization with alkoxides of the alkali metals^{3,4}. It can be said, that by initiation with the lithium compounds in a non-polar medium an isotactic polymer is formed, whereas the use of sodium and potassium compounds leads to an atactic product or a polymer enriched by a syndiotactic component³. The stereospecificity of poly(methyl methacrylates) (*I*) prepared with organometallic compounds of lithium, sodium and potassium in both non-polar and polar media is in principle temperature-independent¹. The effect of the medium upon the stereospecificity of a polymer is characterized by the fact that the non-polar solvent favours the formation of an isotactic structure, whereas the polymer formed in a polar medium is prevalingly syndiotactic. In solutions of medium polarity the equilibrium existing between a complex which favours the formation of an isotactic structure and a complex which controls the propagation to higher contents of syndio-structures leads to the formation of an atactic or a stereoblock polymer^{1,2,5}.

As a rule, linear or cyclic ethers, pyridine *etc.* are used as the polar medium, that is, compounds which contain in their molecule electron donor elements (O, N), capable of participation in the formation of a transient complex which controls the stereospecific introduction of a monomeric unit into a growing polymer chain.

Similarly to the polarity of the medium, the direct presence of electron donor elements in the monomer⁶ molecule also influences the microstructure of polymethacrylates obtained in the presence of butyllithium. During polymerization of methacrylates which contain in their ester group one of the above electron donor elements, the content of the individual stereoisomers in the