MODEL COMPOUNS OF POLY(METHYL METHACRYLATE). CONFORMATIONAL STRUCTURE OF 2,2-DIMETHYL-1-METHOXYPROPANE AND OF THE METHYL ESTER OF 3-METHOXY-2,2-DIMETHYLPROPANOIC ACID

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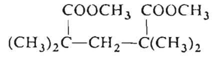
Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

By analysis of infrared, Raman and ^{13}C NMR spectra of 2,2-dimethyl-1-methoxypropane and of the methyl ester of 3-methoxy-2,2-dimethylpropanoic acid, the formation of conformers generated by rotation about the CH_2—OCH_3 and C—CH_2 bonds was studied. It was found that in both molecules, only the form with *trans* orientation of the C—CH_2—O—CH_3 bonds is present. The conformational structure of the major form of the methyl ester of 3-methoxy-2,2-dimethylpropanoic acid was proposed.

Polymers and copolymers containing ester groups are very common, finding widespread technical applications and gaining ground also in medical use. Informations on their conformational structure, which is closely related to their properties, are very meagre. This is partly caused by the circumstance that even the conformational structure of simpler fragments of which these polymers are composed, has not been sufficiently characterized so far. Studies of model compounds can not only contribute to our knowledge of the general rules of conformer generation, but they can also provide the parameters needed for direct studies of polymer conformation.

Informations on the conformational structure in the crystalline state are most often obtained from analysis of X-ray diffraction patterns, frequently in combination with data from infrared spectroscopy. For studies of conformational structure in the liquid state it is often very useful to combine the results of vibrational and NMR spectroscopy. Due to the time-scale of measurement (10^{-12}—10^{-14} s), vibrational spectra practically always represent the sum of the spectra of all conformers present in the measured system. Therefore the measurement of vibrational band intensities in a broad temperature range mostly yields information on the number of conformers present. The geometrical form of the conformers is not easily determined from vibrational spectra, and it can be safely specified only in exceptional cases. On the contrary, NMR spectra of liquid molecules practically always exhibit a single spectrum the parameters of which are the weighted average of the parameters corresponding to the population of various conformers. However, the parameters obtained by analysis of NMR spectra are directly related to the geometrical structure of the molecules. In cases where the number, and possibly also the population of the present conformers are known, the geometrical structure of the various conformers can be directly determined from NMR spectra.

The most common polymer with ester groups is poly(methyl methacrylate) (PMMA). The simplest compound modelling the relation of ester groups in this polymer is the dimethyl ester of 2,2,4,4-tetramethylglutaric acid,

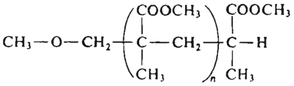


$$(CH_3)_2\underset{}{\overset{COOCH_3}{\overset{|}{C}}}-CH_2-\overset{COOCH_3}{\overset{|}{C}}(CH_3)_2$$

I

the so called "MMA dimer". For this model, the conformers present in the liquid state have been proposed from analysis of vibrational spectra[1-3]. As the results could not be correlated with conformational analysis based on NMR spectra, the conformational structure of the "dimer" (*I*) cannot be regarded as safely determined. For the verification of its conformational structure it is therefore necessary to analyse further molecules containing ester groups.

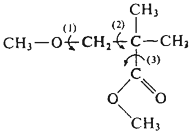
The growth of the PMMA chain during anionic polymerization is modelled by oligomers of the type



$$CH_3-O-CH_2-\left(\underset{CH_3}{\overset{COOCH_3}{C}}-CH_2\right)_n-\underset{CH_3}{\overset{COOCH_3}{C}}-H$$

II

From this series of models, both stereoisomers of the "dimer" with $n = 1$, *i.e.* of the dimethyl ester of 2-methoxymethyl-2,4-dimethylglutaric acid (*II*) have been prepared in pure form in our laboratory, and their configurational structures have been determined by analysis of NMR spectra[3]. Because of the presence of the methoxymethyl group and of the tertiary carbon, conformational analysis of these molecules is even more complicated than that of "dimer" *I*, and it has not been performed so far. As a preparation for the conformational analysis of the stereoisomers of *II*, we have now attempted to perform, by means of NMR and vibrational spectroscopy, the conformational analysis of the methyl ester of 3-methoxy-2,2-dimethylpropanoic acid (*III*).



III

In this molecule, conformers can be generated by rotation about the bonds O—CH_2 (1), CH_2—C (2) and C—(CO) (3); these bonds (1), (2) and (3) are analogous to the rotamer-generating bonds in the „dimer" *II*, and partly also in the "dimer" *I*. The number of conformers which have to be considered with independent rotation about 3 bonds is very large. Therefore some additional data were needed for the conformational analysis of *III*: it was necessary to complete existing data on the NMR and vibrational spectra of methoxyethane, to determine the conformational structure of 2,2-dimethyl-1-methoxypropane and to verify by means of vibrational spectra the conformational structure of the methyl ester of 2,2-dimethylpropanoic acid. In all conformational considerations we have assumed that the ester group is planar and that the ester OCH_3 group assumes *syn* orientation with respect to the carbonyl[4,5] (Fig. 7, 10).

EXPERIMENTAL

Chemicals

Methoxyethane was prepared by continuous etherification of an equimolar mixture of ethanol and methanol by means of sulphuric acid[6] at 413 K. The crude product was obtained by low-temperature rectification on a column with Berl saddles (20 theoretical plates TP), the pure compound was isolated by rectification on a Perkin-Elmer column PE 200 (200 TP) modified for work at low temperatures. B.p. 279·9—280·0 K (uncorrected), literature value[7] 280·7 K. Purity of the product was better than 99·9%. 2,2-dimethyl-1-methoxypropane was synthetized by boiling of a dioxane suspension of a potassium salt of 2,2-dimethyl-1-propanol with methyl iodide[8] for 24 h. After repeated extraction with water and drying by K_2CO_3 the mixture was distilled, dried with $CaCl_2$ and rectified on a PE 200 column. The product (b.p. 342 K uncorr.) contained 99·6% of the compound. Literature values[8,9] b.p. 345·2 K and 344·7 K. The starting 2,2-dimethyl-1-propanol was prepared by the reduction of 2,2-dimethylpropanoyl chloride by tert-butylmagnesium chloride[10].

Methyl ester of 2,2-dimethylpropanoic acid: 2,2-Dimethylpropanoyl chloride (45 g; 373 mmol) was added dropwise to boiling abs. methanol (24 ml; 19·0 g; 592 mmol). The mixture was extracted three times with 20 ml of 10% $NaHCO_3$, twice with 20 ml of water and dried over $CaCl_2$. Distillation on a PE 200 column (b.p. 373·5—375 K uncorr.) yielded 73·3% of compound of 99·95% purity. Literature[11] value b.p. 372·5 K/97·4 kPa.

Methyl ester of 3-methoxy-2,2-dimethylpropanoic acid was prepared by a series of reactions[12].

Methyl-2-bromo-2-methylpropionate (15 g; 83 mmol) and zinc metal (5·11 g; 78 mg atoms) in dry dimethylformal at 313 K yielded the organometal compound to which acetyl chloride (6,14 g; 78 mmol) in dimethylformal (10 ml) was added dropwise at laboratory temperature. After one hour at laboratory temperature the reaction mixture was decomposed by pouring into 500 ml of ice water. The product was extracted with diethyl ether, the extract dried over $MgSO_4$ and the product obtained by rectification on PE 200 column. B.p. 421 K, yield 2 g of compound of 99·16% purity. The starting methyl-2-bromo-2-methylpropionate, dimethylformal and zinc were prepared, purified and dried according to literature[13,14]

Spectrometric Measurements

Raman spectra were measured on the spectrometer Coderg LRDH-800 connected on-line with the multichannel analyzer TN-11 in the Tracor system. Spectra were excited by the line 514·5 nm of the argon laser CR-3 (Coherent Radiation). Spectra were measured in the 90° arrangement and were usually obtained by accumulation of several scans. Low-temperature spectra were measured in a cell with an evacuated jacket. Infrared spectra were measured on the spectrometer Perkin-Elmer 621 and were treated by means of the multichannel analyzer Tracor Northern. Low-temperature spectra were measured in a cell of our own construction[15].

^{13}C NMR spectra were measured on the FT NMR spectrometers FX-60 (JEOL) at 15 MHz and XL-200 (Varian) at 50 MHz. The samples were measured either as neat compounds, or as 50% (v/v) solutions in $CDCl_3$. For the determination of the conformationally sensitive $^3J_{CH}$ coupling constants the spectra were measured with gated irradiation of protons preserving both CH coupling and NOE, or wigh selective irradiation of specific proton groups. In the latter case the real values $^3J_0$ were determined from the experimental values ^3J_R by means of the relation[16,17]

$$^3J_R = [(\Delta\nu - \tfrac{1}{2}{}^3J_0)^2 + (\gamma H_2)^2]^{1/2} - [(\Delta\nu + \tfrac{1}{2}{}^3J_0)^2 + (\gamma H_2)^2]^{1/2}, \qquad (1)$$

where $\Delta\nu$ is the difference of the resonance frequency of the proton interacting with the measured carbon and of the irradiation frequency. The intensity of the irradiation field was determined from $^1J_{CH}$ coupling constants of suitable CH_3 or CH_2 groups in the same molecule, measured with selective irradiation and without it. For easier analysis of complicated multiplets generated by interaction of carbon nuclei with protons over 2 and 3 bonds the resolution was in some cases improved by weighting with a positive exponential and by apodization.

RESULTS AND DISCUSSION

Infrared and Raman Spectra of the Methyl Ester of 3-*Methoxy*-2,2-*dimethylpropanoic Acid*

In Fig. 1 are shown the Raman and infrared spectra of compound *III* in the liquid state (measured at laboratory temperature) and in the glassy state (measured at 143 K). Spectra of the crystalline state are not shown, because in spite of great effort we were unable to induce crystallization of this compound.

As seen from Fig. 1, the bands at 796, 867 and 669 cm^{-1} practically disappear from both infrared and Raman spectra at 143 K. Measurements at various temperatures between 143 and 333 K have shown that the intensities of all these bands change similarly with temperature both in infrared and in Raman spectra. Both infrared and Raman spectra exhibit other temperature-dependent bands, but their temperature changes are less than those of the bands at 796, 867 and 669 cm^{-1}. Such bands are observed in the ranges 1 400 and 1 500, 900 – 1 000 and below 500 cm^{-1}. These bands cannot be used in studies of conformational structure because they either change their intensities mainly in the temperature range where transition from liquid to glassy state takes place, or their temperature dependence differs in infrared and in Raman spectra. Some of these bands are weak or overlapping, so that their temperature dependence is difficult to follow. The spectra also exhibit a number of bands with temperature-independent intensity. Consequently only the bands at 796, 867 and 669 cm^{-1} can be regarded as well-defined conformation-sensitive bands. The temperature changes of vibrational spectra can be most simply explained by the assumption that in the liquid state two conformers are present, and the bands at 796, 867 and 669 cm^{-1} correspond to the energetically less favoured of the two. The other bands correspond either to the energetically more favoured form, or to both forms. It is of course also possible that more than one energetically less favoured forms are present. However, in such a case the ΔH of these forms with respect to the most stable conformer would have to be approximately equal.

If the presence of only two conformers is considered, then the temperature dependence of band intensities can be used for the determination of ΔH. The pairs of bands at 813 and 796 cm^{-1} in Raman spectra, and 880 and 867 cm^{-1} in infrared spectra yield $\Delta H = 2{\cdot}9 \pm 0{\cdot}8$ kJ/mol. The large uncertainty in the determination of ΔH is caused by the small temperature interval available (263 – 333 K). Measurements at lower temperatures were not used for the determination of ΔH because the results of measurements at low temperatures can be modified by kinetic effects (the substance is glassy) or by partial crystallization of the sample.

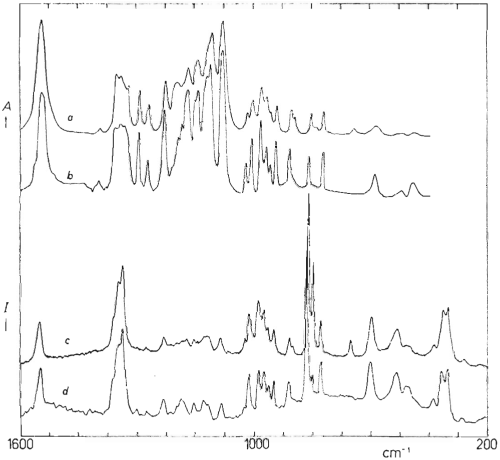


FIG. 1

Infrared (*a*, *b*) and Raman (*c*, *d*) spectra of *III*. *a*, *c* liquid (303 K), *b*, *d* amorphous (143 K)

All bands observed in infrared spectra are also observed in Raman spectra. This indicates that the structure of the major conformer has no symmetry.

In order to assign the groups of bands observed in vibrational spectra to specific conformational structures, the rules of the formation of rotational isomers about the considered 3 types of bonds, (*1*) (*2*) and (*3*), had first to be investigated.

Formation of Rotational Isomers About the Bond O—CH_2

The simplest model of rotational isomerism about the bond (*1*) is methoxyethane. Its infrared and Raman spectra[18-20] and microwave spectra[21,22] in the gaseous and liquid states have been studied in detail and its structure was verified by electron diffraction[23] and semiempirical calculations[24]. All these studies indicate that the dominant conformer corresponds to the structure ***t***; the other possible form is the structure ***g*** (Fig. 2). According to the results of analysis of electron diffraction[23] the bond O—CH_3 in form ***g*** is twisted out of the plane given by the bonds C—C—O by an angle $\Theta_g = 84 \pm 6°$ (Fig. 2). The free energy difference ΔG for these two conformers is determined as 5·17 kJ/mol and the content of the ***t*** form in gaseous state at room temperature[23] is about 80%. The free enthalpy difference ΔH for gaseous methoxyethane[19] was determined from infrared spectra as equal to about 6·3 kJ/mol and in CS_2 solution[20] to about 5·67 kJ/mol. Methoxyethane which is gaseous at room temperature, can be very conveniently studied in sealed cells by Raman spectrometry. In Fig. 3 are shown the Raman spectra of this compound in liquid and crystalline states. At the transition from liquid to crystal, in the whole range of the spectrum, a number of bands is seen to disappear; these bands correspond to the form ***g***. In our study we have concentrated mostly on the band of the O—CH_3 stretching vibration which is very intense in Raman spectra, and which can be easily identified in Raman spectra of all compounds with a methyl ether group. In the liquid state this band is split into a doublet at 852 and 841 cm^{-1}; the component at 841 cm^{-1} disappears at crystallization and is therefore assigned to the structure ***g***. From the temperature dependence of the intensities of these bands we found ΔH 5 kJ/mol.

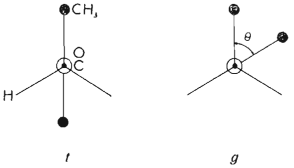


FIG. 2
Conformational structures of methoxyethane

A more closely related model of rotational isomerism on bond (*l*) for the molecule *III* is 2,2-dimethyl-1-methoxypropane, where the methoxymethyl group is bound to quaternary carbon similarly as in *III*. From a comparison of Raman spectra of liquid and crystalline 2,2-dimethyl-1-methoxypropane (Fig. 4) it can be seen that no band of this molecule disappears at crystallization. This indicates the

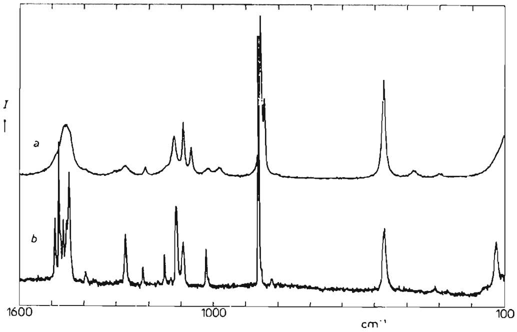


FIG. 3

Raman spectra of methoxyethane *a* liquid, *b* crystal

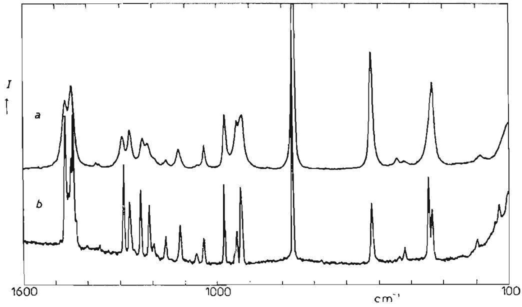


FIG. 4

Raman spectra of 2,2-dimethyl-1-methoxypropane *a* liquid, *b* crystal presence of only a single conformer in liquid 2,2-dimethyl-1-methoxypropane. The band of the O—CH_3 stretching vibration which was used for characterization of rotational isomerism on the O—CH_3 bond in methoxyethane, lies at 764 cm^{-1} in 2,2-dimethyl-1-methoxypropane, and it is a singlet even in the liquid state. In Raman spectra of *III* (Fig. 1*c*) the analogous band of the O—CH_3 stretching vibration is found at 770 cm^{-1} and it is a singlet both in the liquid state, and in the spectrum of the solid state at 143 K. From measurements of Raman spectra it can therefore be concluded that also in the molecule *III* in the liquid state, only the basic rotamer on bond (*1*) is present.

Conformational structure generated by rotation about the bond O—CH_2 can be also followed by means of the $^3J_{CH}$ couplings determined from the fine structure of the carbon signal of the O—CH_3 group in the fully coupled ^{13}C NMR spectrum. For neat methoxyethane at 297 K we found $^3J_{CH_3OCH_2} = 3{\cdot}1$ Hz. The relation between the coupling constant and conformational structure for the staggered forms of methoxyethane ($\Theta_g = 60°$, Fig. 2) is of the form

$$^3J_{CH_3OCH_2} = x_tJ_G + x_g\frac{J_T + J_G}{2}, \qquad (2)$$

where J_T, J_G are the coupling constants for the dihedral angles between the interacting nuclei equal to 180° and 60°, and x_t, x_g are the mol fractions of the corresponding conformers. For an estimate of the parameters J_T, J_G we used the experimental values $^3J_{CH_2OCH_3}$ determined from the ^{13}C NMR spectrum measured with selective irradiation of the methyl protons of the C—CH_3 group. The found value (corrected for the effect of the irradiation field[16,17,25]) $^3J_{CH_2OCH_3} = (1/3) \,.\, (J_T + J_G) = 5{\cdot}3$ Hz. Using this value and the theoretical relation[26] $J_T = 4{\cdot}4J_G$ we obtained $J_T = 10{\cdot}93$, $J_G = 2{\cdot}48$ and $x_t = 0{\cdot}85$. The simplified functional relation $^3J_{CH} = A\cos^2\Theta$, according to which $J_T = 4J_G$, yields for the staggered conformers $J'_T = 10{\cdot}60$, $J'_G = 2{\cdot}65$ and $x'_t = 0{\cdot}89$. For the shape of form ***g*** derived from electron diffraction[23] ($\Theta_g = 84°$), the measured coupling constant $^3J_{CH_3OCH_2} = 3{\cdot}1$ Hz together with the simplified functional relation for $^3J_{CH}$ yields $x''_t = 0{\cdot}91$.

The conformational structure generated by rotation about bond (*1*) in compound *III* was determined similarly from the fine structure of ^{13}C NMR bands. For this compound, both neat and in $CDCl_3$ solution at 298 K, the value $^3J_{CH_3OCH_2} = 2{\cdot}65$ Hz was found, yielding $x_t = 0{\cdot}96$ (with the theoretical relation) or $x'_t = 1{\cdot}00$ (with the simplified relation); at 333 K, $^3J_{CH_3OCH_2} = 2{\cdot}85$ was found, yielding $x_t = 0{\cdot}91$ and $x'_t = 0{\cdot}95$. These results indicate that on bond (*1*), form ***t*** always strongly predominates and that in comparison with methoxyethane, substitution on the carbon in β position with respect to oxygen, leads to a decrease of the population of ***g*** forms on bond (*1*). We also see that especially the values x'_t calculated by means of the simplified relation agree well with the result obtained from Raman spectra, according to which at 298 K compound *III* contains only form ***t***.

Formation of Rotational Isomers About the Bond $CH_2—C$

In our studies of rotation about the bond (*2*) in compound *III*, the staggered rotational isomers shown in Fig. 5 have been considered. Rotation about the bond (*2*) can be followed by means of the coupling of the C-methyl carbon with the CH_2 group protons as manifested in the fine structure of the band of the C-methyl carbon in the fully coupled ^{13}C NMR spectrum. This band (Fig. 6) has the form of the X-band of the system A_2K_3X, yielding by 1st order analysis the value of ${}^3J_{CH_3CCH_3}$, $J_{KX} = 4{\cdot}80$ Hz, and the value of ${}^3J_{CH_3CCH_2}$, $J_{AX} = 3{\cdot}27$ Hz for a 50% v/v solution in $CDCl_3$ at 298 K, and $J_{AX} = 3{\cdot}37$ Hz both for the neat compound and the solution at 333 K. In the simplest approach, neglecting the effect of orientation of substituents[26-29] on the values of the parameter J_T, J_G, the relation between the coupling constant J_{AX} and the rotational isomers on bond (*3*) is given by the relation

$$2J_{AX} = x_T(J_T + J_G) + (1/2)\,x_G(J_T + 3J_G)\,. \qquad (3a)$$

For $x_T = 1 - x_G$, $J_T + J_G = \sum J$, $J_T - J_G = \Delta J$, then

$$x_G = 2\,\frac{\sum J - 2J_{AX}}{\Delta J}\,. \qquad (3b)$$

The values of J_T, J_G for the studied fragment, with rather complicated substitution, are not known. The effect of substituents in dependence on their electronegativity and position in the interaction pathway upon values of J_{CH} has been studied in great detail by Spoormaker and coworkers[30,31], who derived a system of additive increments also for ${}^3J_{CH}$; by means of this system of additive increments it is possible to estimate the values of J_T, J_G in some substituted fragments. For the unsubstituted fragment $^{13}C^{\alpha}—C^{\beta}—C^{\gamma}H_3$ these authors give the value ${}^3J(^{13}C—H) = 5{\cdot}8$ Hz. Substitution by methyl in β-position decreases this value by 0·57 Hz, substitution by OH in γ-position by 1·2 Hz, substitution by —OH in α-position has negligible effect. The validity of these increments for the molecule *III* can be verified by means of the experimental values of ${}^3J_{CH_3CCH_3}$ and ${}^3J_{CH_2CCH_3}$ which are both conformationally independent and equal to $(1/3)(J_T + J_G)$, in the first case with the groups CH_2, CO in β-position, in the other case with CH_3, CO, in β position and with $—OCH_3$ in α-position. For both these couplings we have determined ${}^3J_{CH} = 4{\cdot}8$ Hz, *i.e.* lower by 1 Hz as compared to ${}^3J_{CH} = 5{\cdot}8$ Hz for the unsubstituted fragment[30,31]. From this it is evident that the substitution effect of CH_2 and CH_3 groups is similar; also the combined effect of β-CO and α-OCH_3 groups does not differ much from the sum of the increments of the β-CH_3 and α-OH groups as proposed by Spoormaker. We assume that the effect of the O—CH_3 group in α-position is probably negligible,

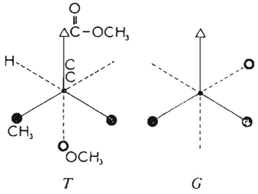


FIG. 5

Conformers of *III* generated by rotation about bond (2)

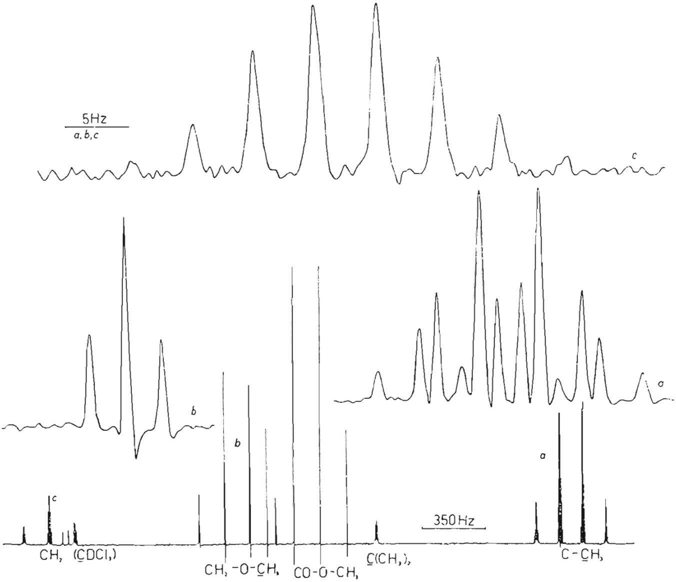


FIG. 6

^{13}C NMR spectra (50 MHz) of *III*, 50% w/v in $CDCl_3$, 298 K, fully coupled, with NOE similarly as observed by Spoormaker for the —OH substituent. As an estimate of the parameters J_T, J_G for the conformationally dependent coupling path CH_3CCH_2 we used the basic value 4·8 Hz accounting for substitution by CH_3 and CO in β-position; as a correction accounting for substitution by OCH_3 in γ-position we used the increment proposed by Spoormaker for γ substitution by —OH *i.e.* 1·2 Hz. In this way we obtained the value $(1/3)(J_T + J_G) = 3{\cdot}6$ Hz, in good agreement with the value 3·5 ± 0·2 Hz found[31] for 2,2-dimethyl-1-methoxypropane by Spoormaker. Using the theoretical relation[26] $J_T = 4{\cdot}4J_G$ we obtain for the studied fragment $J_T = 7{\cdot}4$ $J_G = 1{\cdot}7$ Hz, and using the simplified relation $J_T = 4J_G$ we obtain $J'_T = 7{\cdot}2$, $J'_G = 1{\cdot}8$ Hz. The values of x_G, x'_G calculated from the experimental values of J_{AX} by both procedures are shown in Table I. Considering with Spoormaker the error ±0·2 Hz in the determination of $(1/3)(J_T + J_G)$, then the found values of x_G should be correct within ±0·12. From Table I we see that with both computing procedures, form ***G*** is indicated as the major form generated by rotation about bond (*2*).

The relatively small experimentally accessible temperature range of ^{13}C NMR does not permit a determination of the free energy difference between the forms ***T*** and ***G***. The circumstance that a temperature change in this very limited range is measurable at all indicates that ΔG is neither very small nor very large but is expected to lie in the range of values corresponding to a maximum temperature change of populations (2·1 – 5 kJ/mol).

Rotation About the Bond C—(CO)

For methyl esters it is usually assumed[32] that the major conformers generated by rotation about the C—(CO) bond in the staggered approximation have the carbonyl in *syn* orientaton with respect to some substituent on the neighbouring carbon atom[33] (*syn*-form, Fig. 7). Theoretical calculations have shown[34] that in poly (methyl methacrylate) the conformer with *anti* orientation of the carbonyl with respect to substituents on the neighbouring carbon (*anti*-form Fig. 7) can also

TABLE I
Content of form ***G*** in compound *III*

K	J_{AX}	x_G	x'_G
		(±0·12)	
298	3·27	0·89	0·91
330	3·37	0·83	0·84

appear as a minor component. ΔH of *anti*-form related to *syn*-form was calculated as 8 kJ/mol.

In order to find out if *anti* forms *a* can also appear in simple esters with quaternary carbon next to carbonyl we have measured vibrational spectra of the methyl ester of 2,2-dimethylpropanoic acid. The measurements have shown that in the Raman spectrum of the methyl ester of 2,2-dimethylpropanoic acid the band at 737 cm^{-1} (Fig. 8) disappears at crystallization; this band can evidently be assigned to *anti*-form in the staggered approximation. The temperature dependence of the relative intensities of this band and of the band at 757 cm^{-1} yields ΔH 8 kJ/mol. As in the infrared and Raman spectra of the methyl ester of 2,2-dimethylpropanoic acid only one band disappearing at crystallization could be detected and its intensity is very low (it cannot be detected in normal measurements without accumulation) it can be concluded

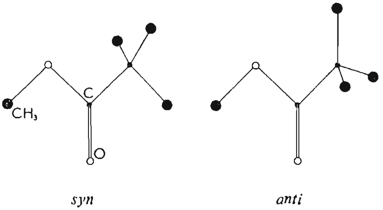


FIG. 7

Conformers of the methyl ester of 2,2-dimethylpropanoic acid generated by rotation about bond (*3*)

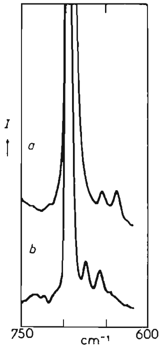


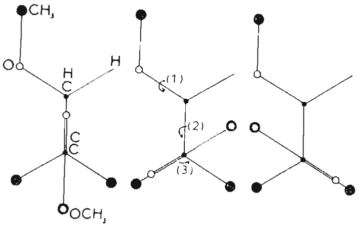
FIG. 8

Raman spectra of the methyl ester of 2,2-dimethylpropanoic acid in the range 600 to 750 cm^{-1} *a* liquid, *b* crystal that the population of the *anti*-form is very low, in agreement with the value of ΔH and with the theoretical calculations. As the intensity of the three conformationally sensitive bands of *III* is relatively high and as their temperature dependence corresponds to $\Delta H = 2{\cdot}9 \pm 0{\cdot}8$ kJ/mol, we assume that the presence of *anti*-forms cannot account for the behaviour of the conformationally sensitive bands in the vibrational spectra of *III*.

By rotation about bond (*3*) in compound *III*, three different *syn*-forms can be generated (*syn*-CH_2, *syn*-CH_3^1 and *syn*-CH_3^2, Fig. 9).

As compound *III* could not be crystallized, and from model compounds manifestations of forms *syn*-CH_2 and *syn*-CH_3 are not known, it cannot be decided from vibrational spectra if some of the conformationally sensitive bands of *III* could be characteristic of rotation about bond (*3*).

In studies of rotation about bond (*3*) it has to be considered that in Raman spectra measured with perpendicular polarization, the C=O stretching vibration lies at 1 738 cm^{-1}, and with parallel polarization it lies at 1 734 cm^{-1}. The difference of these two wavenumbers indicates that in *III*, resonance interaction between transi-



S-CH_2 S-CH_3^1 S-CH_2^1

FIG. 9

Conformers generated by rotation about bond (*3*) in compound *III* with structures (t) (G) on bonds (*1*) (*2*)

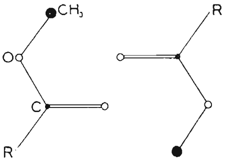


FIG. 10

Form of association of ester groups

tion dipoles of different molecules takes place; in other simple esters such interaction is connected with the formation of ordered structures generated by interaction of dipole moments of ester groups[35] (Fig. 10).

In *III*, organized structures of the type shown in Fig. 10 can be generated for all *syn*-forms on bond (*3*), if ***T*** structure exists on bond (*2*). With ***G*** structure on bond (*2*), the aggregate can be formed without hindrance with both forms *syn*-CH_3, but steric hindrance appears with form *syn*-CH_2. Considering only the preferred forms on bonds (*1*) and (*2*), (***t***) (***G***), then two O—C bonds lie parallel in the conformer (***t***) (***G***) (*syn*-CH_3^2) (Fig. 9), which might lead to a lower probability of this conformer.

CONCLUSIONS

A comparison of the results of analysis of NMR spectra and of measurements of vibrational spectra indicates that in the methyl ethers of the type $C^{\beta}—C^{\alpha}H_2—$ $—O—CH_3$, the presence of the trisubstituted carbon β decreases the probability of occurrence of the out-of-plane conformation of the bonds $CH_3—O—CH_2—C$ both in 2,2-dimethyl-1-methoxypropane and in molecule *III* to such an extent that in their conformational analysis only the planar form ***t*** (Fig. 2) need be considered. Analysis of NMR spectra indicates that by rotation about the bond CH_2-C in compound *III*, form ***G*** (Fig. 5) is generated as the major structure; its content at room temperature is 80 to 95%. From NMR spectra, ΔG of form ***T*** lies in the range 2·1 to 5 kJ/mol. The intensities and ΔH of conformationally sensitive bands of *III* in vibrational spectra indicate that at least one but possibly all three conformationally sensitive bands correspond to temperature changes of the population of form ***T*** on bond (*2*); from vibrational spectra, the population of this form in the glassy state at 143 K is negligible.

Similarly as other low-molecular weight esters[3], also *III* is found to form ordered structures in the liquid state. At a high population of form ***G*** this indicates that the form (***t***)(***G***)(*syn*-CH_3^1) (Fig. 9) is highly populated in the liquid state. In order to decide if all bands observed in the vibrational spectrum of the glassy state measured at 143 K correspond to this conformer, or if other structures generated by rotation about the bond C—(CO) (Fig. 9) are also present at this temperature, it will be necessary to measure further models in which forms with *syn* orientation both of CH_2, and of CH_3 groups groups with respect to carbonyl can be formed.

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