

RAMAN AND INFRARED SPECTRA AND THE STRUCTURE OF THE DIMETHYL ESTER OF 2,2,4,4-TETRAMETHYLGLUTARIC ACID

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Raman and infrared spectra of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid in the solid and liquid states and the temperature dependence of the spectra were measured. The behaviour of some bands in the spectra indicates the presence of three conformers in the liquid state. Local order of the molecules due to dipolar interactions of ester groups was observed.

In our preceding paper¹ we have studied, by means of infrared spectra, the conformational structure of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid (further only "ester", if not indicated otherwise). In the solid state, the dichroism of infrared bands indicates the presence of only a single conformer to which the *trans* structure of the carbon chain in the staggered approximation was assigned. In the liquid state a new band appears in the infrared spectrum, indicating the presence of a further stable conformer. Based on the analysis of infrared spectra of deuterio derivatives of the ester, and on the structure of similar model compounds, the *gauche* structure of the carbon chain in the staggered approximation was assigned to this conformer. In this structure, two conformations are possible for one of the ester groups, differing in the mutual orientation of the C=O bond and of the methylene. It was not possible to decide about the presence of these conformers in the liquid ester from infrared spectra measured at a single temperature.

As the dimethyl ester of 2,2,4,4-tetramethylglutaric acid is an important low-molecular-weight model for studies of the structure of poly(methyl methacrylate), we have attempted to refine the determination of its conformational structure by analysis of the Raman spectra of the ester in the solid and liquid states and of the temperature dependence of its Raman and infrared spectra. We have also followed the effect of temperature and solvents on the wavenumber and shape of the band of the C=O stretching vibration. The wavenumber difference of the carbonyl band in the anisotropic and isotropic components of Raman scattering can indicate the presence of molecular local order in the liquid state caused by strong dipole-dipole interactions², such as was detected in the case of methyl acetate and of other simple esters³.

EXPERIMENTAL

Preparation and purity of samples were the same as in our preceding paper¹. 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). The spectra of samples in capillary cells were measured in the 90° arrangement. The temperature dependences of Raman spectra were obtained by heating the cells with the sample by multiple accumulation.

Infrared spectra were measured on the spectrometer Perkin-Elmer 580B, connected on-line with the multichannel analyzer TN-4000 (Tracor Northern). Spectra were measured by the KBr method. The temperature dependences were measured in the commercial Perkin-Elmer heated cell.

RESULTS AND DISCUSSION

Infrared spectra. Comparison of infrared spectra (Fig. 1) of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid in the crystalline state (at 298 K) and in the liquid

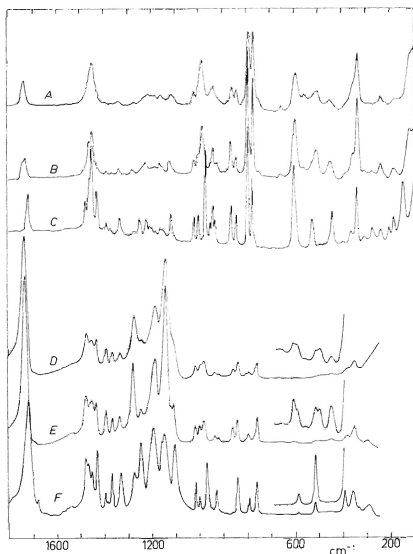


FIG. 1

Raman spectra (A liquid ester at 451 K, B liquid ester at 303 K, C crystalline ester at 298 K) and infrared spectra (D liquid ester at 478 K, E liquid ester at 303 K, F crystalline ester at 298 K)

state (at 303 and 478 K) reveals the appearance of some new bands ($925, 884, 813, 659, 612, 562$ and 502 cm^{-1}) in the liquid state. According to their temperature behaviour these bands can be divided into those with intensity decreasing with decreasing temperature ($813, 659, 562$ and 502 cm^{-1}), and those with intensity increasing with decreasing temperature (925 and 612 cm^{-1}). For the band at 884 cm^{-1} which disappears upon crystallization, the character of the temperature dependence cannot be determined because of its low intensity. In the doublet $520, 502\text{ cm}^{-1}$, the intensity of the component which is present in the crystalline state (520 cm^{-1}) increases with decreasing temperature, but in the doublet $612, 595\text{ cm}^{-1}$, the intensity of the analogous band (595 cm^{-1}) decreases. The bands 944 and 866 cm^{-1} appear in the spectra of both liquid and crystalline ester, but their intensity is much lower (about ten times) in the crystalline state. The intensity of the band at 866 cm^{-1} evidently increases with decreasing temperature.

Raman spectra. Also the Raman spectrum of the liquid ester (at 303 and 451 K) exhibits bands which were not observed in the spectrum of the crystalline substance at 298 K ($925, 884, 813, 659, 562$ and 502 cm^{-1}) (Fig. 2). The intensity of the bands $884, 813, 659$ and 562 cm^{-1} decreases with decreasing temperature, the intensity of the band 925 cm^{-1} increases with decreasing temperature, for the band at 502 cm^{-1} the character of the temperature behaviour cannot be safely determined because of overlap with the band 520 cm^{-1} . The intensities of bands which in the infrared

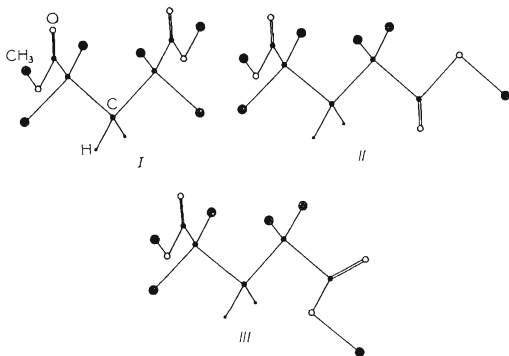


FIG. 2

Conformational structures of the ester

spectrum decrease markedly upon transition from liquid to crystalline state (944 and 866 cm^{-1}), remain comparable in the Raman spectrum. Similarly the intensity of the band 454 cm^{-1} does not change in the Raman spectrum, although in the infrared spectrum of the crystalline ester this band does not appear. The intensity of the band at 866 cm^{-1} increases with decreasing temperature.

Conformational Structure of the Ester

In ref.¹ it was shown that the crystalline ester contains a single conformer with a planar structure of the carbon backbone with ester groups on opposite sides of the chain (**T**), while both ester groups have the same conformational structure, with a *gauche* (**g**) arrangement of the bonds $\text{CH}_2\text{—C}(\text{CH}_3)_2\text{—CO—O}$. This conformer is designated as **T_g** (Fig. 2, I). We assume that also in the liquid state the form **T_g** is the most favourable energetically. As both the infrared and the Raman spectrum of the liquid ester exhibit two groups of bands which disappear at crystallization, with an opposite temperature dependence of intensities, at least two other conformers, in addition to **T_g**, have to be considered in the interpretation of spectra of the liquid ester. The planar structure of the carbon backbone **T** permits only *gauche* forms of the ester groups on steric grounds. However with a *gauche* form of the carbon backbone which was proposed¹ as a further stable form of the carbon backbone in the liquid ester, one of the two ester groups can assume either of two forms, *trans* (**G_t**, Fig. 2, II) or *gauche* (**G_g**, Fig. 2, III). The measured temperature dependence of band intensities in infrared and Raman spectra can be explained by the presence of three conformational structures **T_g**, **G_t** and **G_g** in the liquid state, if some vibrational modes are sensitive to the skeletal conformational transition $\text{T} \leftrightarrow \text{G}$, and other to the ester conformational transition *trans* \leftrightarrow *gauche*. If we assume that the form **T_g** is energetically the most favoured, then the conformationally sensitive bands can be assigned to the three conformers. In the doublet 612 and 595 cm^{-1} , the intensity of the band which disappears at crystallization (612 cm^{-1}) increases with decreasing temperature, while the intensity of the band at 595 cm^{-1} which persists in the crystalline state, decreases with decreasing temperature. In the case of a system of three conformers such temperature dependence can only appear when the band of the energetically most favoured conformer at 595 cm^{-1} (**T_g**) is overlapped by a band of the least favoured conformer (**G_g** or **G_t**) and the band at 612 cm^{-1} appears only in the spectrum of the remaining conformer (**G_t** or **G_g**).

It is not possible to determine safely from vibrational spectra which of the forms **G_g** and **G_t** is energetically more favoured, but as in the form **G_g** the methyl group lies in the plane of the ester group, and in the form **T_g** only this position of the ester group is permitted on steric grounds, we assume that the bands of the forms **T_g** and **G_g** overlap at 595 cm^{-1} , and the doublet component at 612 cm^{-1} corresponds to the form **G_t**. Therefore this doublet is probably sensitive to the conformational

transition *trans* \leftrightarrow *gauche*, and the temperature dependence of the intensities of the doublet components indicates that the form G_g is the least favoured energetically. The decrease of the intensity of the band at 595 cm^{-1} with decreasing temperature in the studied temperature range is caused by the circumstance that the loss of the intensity of the band of form G_g at 595 cm^{-1} is more rapid than the gain of intensity of the band of form T_g ; this can happen when the energy difference between T_g and G_i is smaller than between G_i and G_g .

The other temperature dependent bands can be assigned by a similar procedure. Thus the analysis of the temperature dependence indicates that in the doublet 520 and 502 cm^{-1} , the band at 520 cm^{-1} corresponds to the form T_g and the band at 502 cm^{-1} to G_g ; therefore this doublet is sensitive to the conformational transition $T \leftrightarrow G$. The band at 925 cm^{-1} behaves similarly as the band at 612 cm^{-1} and it is therefore assigned to the form G_i . The bands at 884 , 813 , 659 and 562 cm^{-1} are characteristic of the skeletal structure G , but it cannot be decided if they appear in the spectra of both conformational forms G_g and G_i , or only in the spectrum of form G_g . For this it is necessary to determine the enthalpy differences between the three conformers; in the studied three-component system, the enthalpy differences could not be determined from the measured temperature dependence of the spectra because of band overlap.

Interesting is the behaviour of the band at 866 cm^{-1} the intensity of which in the infrared spectrum decreases appreciably at crystallization. As in the Raman spectra the intensity of this band remains comparable in the crystalline and liquid states, it cannot be included among the bands disappearing at crystallization¹. The band appears probably only in the spectrum of the form T_g , because its intensity increases with decreasing temperature. As in the crystalline state the molecule of the ester has the structure T_g with C_2 symmetry, the mentioned decrease of the band intensity in the infrared spectrum is probably caused by a change in the activity of some vibrations due to the symmetry of the crystalline cell. A similar behaviour was observed also for the bands at 944 and 454 cm^{-1} .

C=O Stretching Vibration

The band of the C=O stretching vibration in Raman and infrared spectra of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid has a complicated shape which changes in various solvents and with temperature, with a simultaneous shift of band wavenumber.

In the infrared spectrum of the solution of the ester in hexane the carbonyl band has the shape of a doublet with a 1 : 1 intensity and wavenumber difference 4.5 cm^{-1} . In infrared spectra of other solutions (CCl_4 , CH_3CN , toluene, benzene, chloroform), rather symmetrical carbonyl bands are observed, of width greater than in hexane.

The carbonyl band evidently also consists of two components, but these cannot be resolved in the spectrum because of their larger width.

We have measured the carbonyl band of the ester both in the isotropic and in the anisotropic component of Raman scattering for the neat compound at 303 K (Fig. 3) and 451 K and in CCl_4 and CH_3CN solutions (12.5% by weight) at room temperature. The band has a clearly asymmetric shape, and this asymmetry is more pronounced in the isotropic component of Raman scattering. In all cases the band lies at a higher wavenumber in the anisotropic component of Raman scattering, than in the isotropic component. At 303 K, the wavenumber difference $\Delta\nu = \nu_{\text{aniso}} - \nu_{\text{iso}}$ is about 6.5 cm^{-1} , at 451 K about 2.5 cm^{-1} and in the studied solutions about $1-2 \text{ cm}^{-1}$. The wavenumber of the carbonyl band in the isotropic component of Raman scattering corresponds to the wavenumber in the infrared spectrum.

The shape of the $\text{C}=\text{O}$ stretching vibration in infrared spectra could be explained by the existence of the conformational forms of the ester. However, this explanation cannot be valid for the interpretation of the wavenumber difference $\Delta\nu$ of the carbonyl band in the isotropic and anisotropic components of Raman scattering. Upon dilution of the ester in solvents $\Delta\nu$ decreases so strongly that this cannot be explained by changes of conformer populations.

For $\text{C}=\text{O}$ stretching vibrations, the wavenumber difference ($\Delta\nu$) in isotropic and anisotropic components of Raman scattering is caused by transition dipole-transition dipole interaction of these bonds². When local order is absent, the effect of dipole-dipole interaction is manifested by the position of the band of the stretching vibration of this bond in the anisotropic component of Raman scattering⁴. For simple

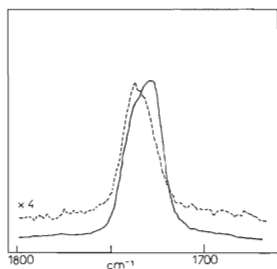


FIG. 3

Carbonyl band of the ester in the isotropic (—) and anisotropic (·····) component of Raman scattering at 303 K

esters we have found that the position of the C=O stretching band in isotropic Raman scattering is shifted due to transition dipole interactions, proving the presence of molecular local order³.

The concentration and temperature dependences of $\Delta\nu$ in Raman spectra of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid are quite analogous to the behaviour of C=O stretching bands in simple esters, and the agreement of the wavenumbers of the carbonyl band in infrared spectra and in the anisotropic component of Raman scattering (they differ by 1 cm^{-1} at most) indicates³ that the transition dipole interaction also causes a band shift in the isotropic component of Raman scattering in the case of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid. Therefore we assume that in the liquid state of the studied ester, similarly as in other simple esters³, $\Delta\nu$ is given by intermolecular transition dipole-transition dipole interactions indicating that molecular local order caused by dipolar interactions of ester groups exists in the liquid state of the studied ester.

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