Dipole–dipole interactions in simple esters and in liquid-crystal polyesters

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The C=O stretching frequencies of alkyl esters and polyesters are used as a probe to study the possible existence and the extent of dipole–dipole interactions between ester groups in these systems. The dynamics of a linear array of electric dipoles is worked out. The results account for the observed infra-red and Raman spectra of solid methyl acetate and ethyl acetate, but fail to account for the multiplet structure observed for one of the polyesters, which shows liquid-crystalline properties. Calculations show that the vibrational spectra are a good probe only of intermolecular interactions at short range.

(Keywords: dipole interactions; esters; polyesters; liquid crystal; dynamics; infra-red spectra; Raman spectra; modelling)

INTRODUCTION

In a recent paper[1] some of us have reported on the temperature dependence of the infra-red spectrum of a liquid-crystal polyester $[-(CH_2)_{10}-OOC(C_6H_4)OOC(C_6H_4)COO(C_6H_4)COO-]_n$, hereafter referred to as HTH-10. This liquid-crystal polymer is part of a large class of compounds first prepared by Ober *et al.*[2] and later by the group of Chiellini[3]. The spectrum reported again in *Figure 1* shows in the region of the C=O stretching an interesting temperature-dependent fine structure, which evolves from the K through S to I phases. We thought that such spectroscopic fine structure might help in the understanding of the nature of the peculiar intermolecular interactions that induce the liquid-crystalline phase.

Our main interest is to use the stretching of the carbonyl group as a probe for exploring the intermolecular interactions that may occur between these kinds of molecules. In particular, our aim is to probe whether and to what extent the ester group is involved in dipole–dipole interactions with neighbouring groups.

In this work we first collect experimental infra-red and Raman data and examine the vibrational characteristic of the C=O groups in several simple esters as model compounds. Then, with the use of quantum-chemical calculations, we predict what may happen to the vibrational modes of the C=O group when electric dipoles approach the C=O group from either side. Then we calculate the vibrations of an infinite chain of interacting dipoles in various geometries. The results are compared with the experimental observations on model compounds. The method is then applied to the case of the liquid-crystal polyester HTH-10.

DIPOLE–DIPOLE INTERACTIONS AND VIBRATIONAL PERTURBATION OF THE C=O GROUP IN METHYL ACETATE

We have first taken methyl acetate as a model compound and have calculated the minimum-energy geometry and dipole moment by MNDO (modified neglect of differential overlap) semiempirical quantum-chemical methods[4]. After suitable energy minimization, the calculated equilibrium molecular geometry is given in *Figure 2a.* The molecule is polar with a calculated equilibrium electric dipole moment $|M| = 1.748$ D. The dipole practically lies along the C=O bond. Calculations give the C=O bond length $r_{C=O} = 1.228$ Å and a vibrational frequency $\nu_{C=O} = 2109\ cm^{-1}$, with a dipole moment change $\partial\mu/\partial r_{C=O} = 4.678$ D Å^{-1}. The calculated point charges on the O and C atoms are -0.356 and $+0.348$ electrons respectively. Then we bring up to the molecule on either side two large static and unpolarizable dipoles (5.5 D) kept at a fixed distance $r_{C=O}$/dipole = 6 Å and lying in the same plane as the C=O group, the plane being orthogonal to the molecular plane. After energy minimization of the new system (*Figure 2b*) $r_{C=O} = 1.254$ Å, $\nu_{C=O} = 2074\ cm^{-1}$, $q_O = -0.391e$ and $q_C = +0.352e$.

For the purpose of our work, we do not need to carry out the traditional scaling of the calculated force constants to reach the fitting between calculated and experimental C=O stretching frequencies[5]. The relevant message we derive from these quantum-chemical calculations is that dipole–dipole interactions occurring within reasonable distances *lengthen* the C=O bond, *decrease* the bond order, *increase* the electronic charge on the oxygen atom and *lower* the vibrational frequency.

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THE EXPERIMENTAL VIBRATIONAL SPECTRA OF SIMPLE ALIPHATIC ESTERS

As a check of the above theoretical predictions, we have recorded the vibrational infra-red and Raman spectra of several model molecules of polyesters, namely of the series of CH_3–COO–$(CH_2)_nCH_3$ where $n=0$ to 11. We refer to another paper for a detailed discussion of the experimental aspects as well as of the vibrational assignment of these molecules[6]. In this work we focus our attention only on the vibration of the structural probe we decided to use, i.e. on the stretching(s) of the C=O group(s), which give(s) rise to strong bands near 1700 cm^{-1} and whose assignment is unquestionably clear and certain.

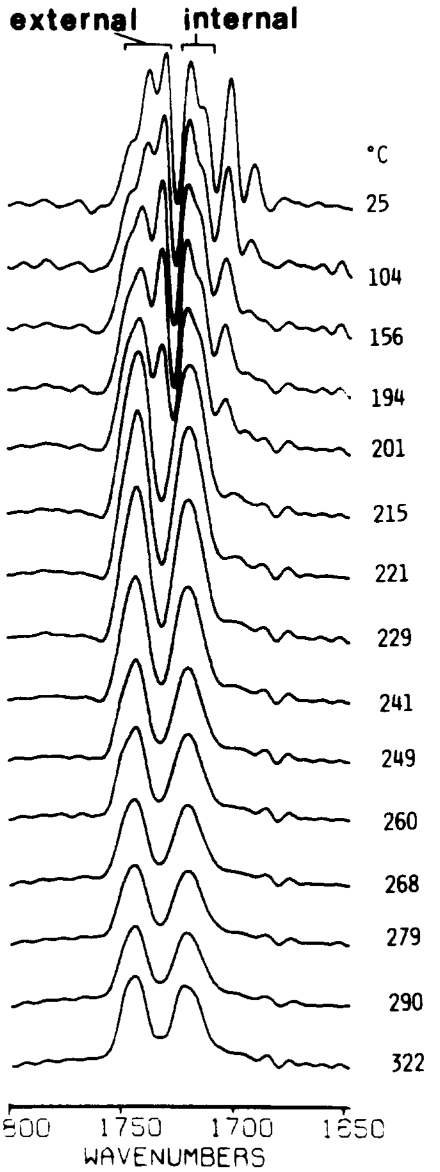

Figure 1 Temperature dependence of the deconvoluted infra-red spectrum of HTH-10 in the C=O stretching region

The ability of the C=O group to probe its environment can be tested when the spectra of each compound are measured in the gas, liquid and solid phases. While in the gas phase molecules can be considered to be non-interacting, in the liquid phase molecules are approaching each other and each oscillator feels an average electrostatic interaction with the neighbouring molecules. In the solid crystalline phase highly directional dipole–dipole forces at van der Waals distances act between C=O groups, in a way very similar to that mimicked by our quantum-chemical calculations.

The observed vibrational frequencies of the compounds studied are plotted in *Figure 3 versus* the number of CH_2 units in the alkyl chain. The vibrational frequencies in *Figure 3* can be approximately grouped in three frequency ranges for the three phases:

gas phase	$\nu_{C=O} > 1760\,cm^{-1}$
liquid phase	$\nu_{C=O}$ between 1750 and 1740 cm^{-1}
solid phase	$\nu_{C=O}$ between 1730 and 1720 cm^{-1}

These observations agree with calculations which predict that $\nu_{C=O}$ should decrease when interactions become larger since dipoles move closer.

The comparison of i.r. and Raman spectra of liquid and solid samples provides us with additional useful information. While the i.r. and Raman frequencies of the liquid samples are practically coincident, as expected, the C=O stretchings for the simplest molecules in the solid state occur at different frequencies in the i.r. and Raman spectra. The distance of this i.r./Raman doublet is non-negligible especially for methyl acetate and ethyl acetate. It is very likely that these two systems crystallize more easily and better since they are not perturbed much by the conformational flexibility, which, instead, becomes more and more complex with longer alkyl chain. The observed i.r./Raman splitting for crystalline methyl acetate and ethyl acetate is 1738–1723 cm^{-1} ($\Delta\nu = 15$ cm^{-1}) and 1732–1724 cm^{-1} ($\Delta\nu = 8$ cm^{-1}) respectively.

The observation of a splitting with i.r. and Raman non-coincidence suggests the existence in the unit cell of at least two molecules with a centre of symmetry between

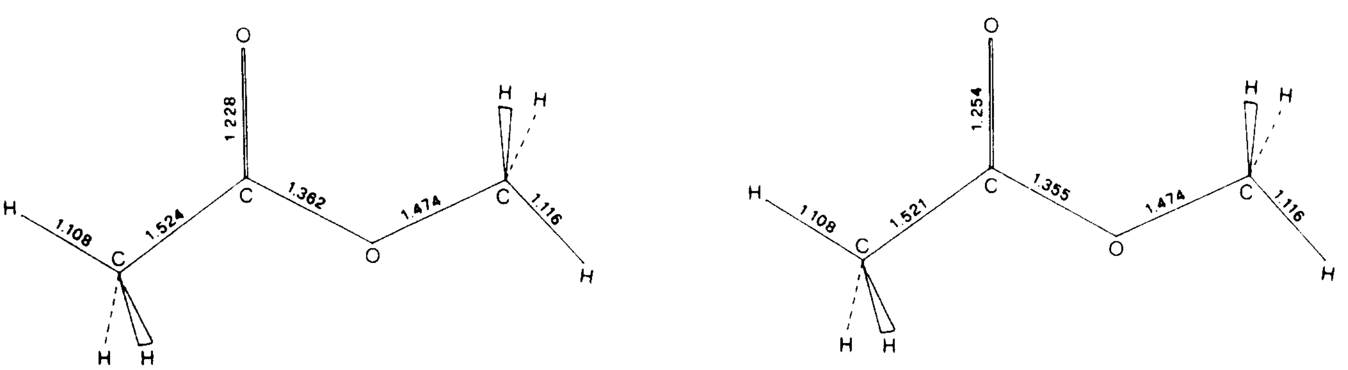

Figure 2 (a) MNDO minimum-energy structure of methyl acetate *in vacuo*. (b) MNDO minimum-energy structure of methyl acetate whose C=O groups are sandwiched between fixed and unpolarizable dipoles of 5.5 D at a fixed distance of 6.0 Å

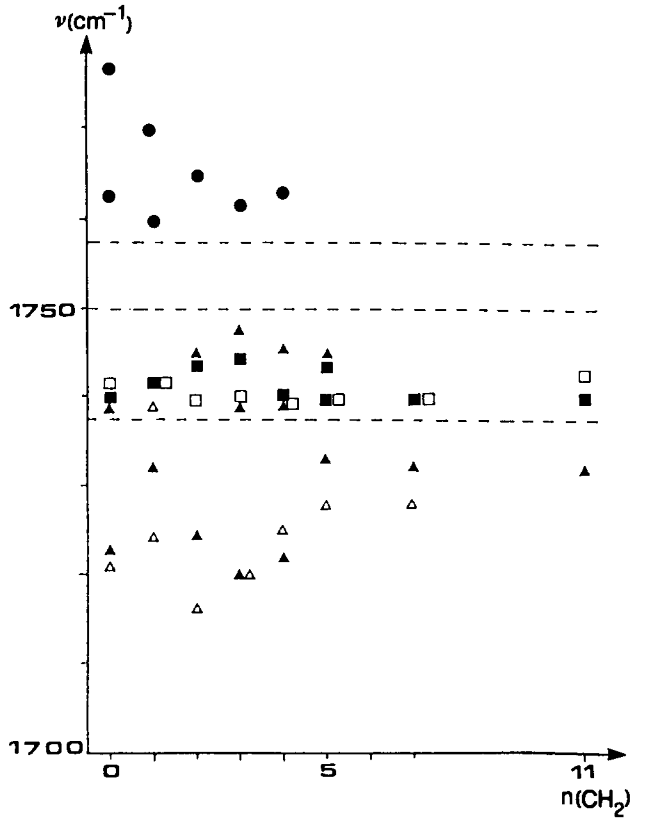

Figure 3 Vibrational frequencies of the C═O stretching mode in the infra-red and Raman spectra of a series of aliphatic esters CH_3COO–$(CH_2)_n$–CH_3 with $n = 0$–11. Infra-red: gas (●), liquid (■), solid (▲). Raman: liquid (□), solid (△). For a discussion of the choice of the bands and of the experimental aspects of this spectroscopy see ref. 6

the two C═O dipoles necessarily facing each other in an antiparallel way. The observed modes are then the antisymmetric *ungerade* (i.r.-active) and the symmetric *gerade* (Raman-active) C═O stretchings.

We may consider the observed splitting as the result of dipole–dipole interactions between the two C═O groups placed at an as yet unknown distance d. No structural data from X-ray scattering are so far available for these two substances in the crystalline state.

THE VIBRATIONS OF AN ARRAY OF DIPOLES

One possible way to account for the observed splittings is to consider the dynamics of a set of dipoles facing each other in some particular geometry. We develop here a simple model that may account for the experimental observations for the simple esters and may eventually be extended for understanding the spectroscopic splitting observed in the i.r. spectra of the complex liquid crystals such as that presented in the first section of this paper.

Let us consider an infinite array of dipoles assumed to be kinetically uncoupled, but interacting through dipole–dipole forces. The expression for the potential energy of the interaction between two dipoles $\boldsymbol{M}_A$ and $\boldsymbol{M}_B$ in any position in space is given by:

$$V = -(|\boldsymbol{M}_A||\boldsymbol{M}_B|/d^3)[2\cos\Theta_A\cos\Theta_B - \sin\Theta_A\sin\Theta_B\cos(\varphi_A-\varphi_B)] \tag{1}$$

where d is the distance between the two dipoles, and the angles Θ_A and Θ_B define the mutual orientation of the dipoles with respect to the given coordinate system[7].

The second-order term in the Taylor expansion of V in terms of the variable r yields the expression for the interaction force constant:

$$f_{rr} = (\partial^2 V/\partial r^2)_{eq} \tag{2}$$

$$f_{rr} = (|\partial \boldsymbol{M}_A/\partial r||\partial \boldsymbol{M}_B/\partial r|/d_{AB}^3)[2\cos\Theta_A\cos\Theta_B - \sin\Theta_A\sin\Theta_B\cos(\varphi_A-\varphi_B)] \tag{3}$$

This approach has already been adopted by Krimm *et al.*[8] and by Bosi *et al.*[9] in treating the C═O/C═O interactions in carboxylic acid dimers.

For an infinite array of molecular units when Born–Von Karman cyclic boundary conditions are taken into account, the eigenvalue equation to be solved using Wilson's internal coordinates[10] can be written in terms of the wavevector $\boldsymbol{k}$ as follows[11]:

$$\boldsymbol{G}_R(\boldsymbol{k})\boldsymbol{F}_R(\boldsymbol{k})\boldsymbol{L}(\boldsymbol{k}) - \boldsymbol{L}(\boldsymbol{k})\Lambda(\boldsymbol{k}) \tag{4}$$

where $\boldsymbol{L}(\boldsymbol{k})$ is the $\boldsymbol{k}$-dependent matrix of vibrational amplitudes and Λ is the diagonal matrix of eigenvalues, which provides the vibrational frequencies ν_i (cm^{-1})$=1302\lambda_i^{1/2}$. In equation (4) $\boldsymbol{G}_R$ and $\boldsymbol{F}_R$ are the $\boldsymbol{k}$-dependent kinetic and potential energy matrices respectively, which can be written as:

$$\boldsymbol{G}_R(\boldsymbol{k}) = \boldsymbol{G}_R^{(0)} + \sum_s \boldsymbol{G}_R^{(s)} e^{iks} \tag{5}$$

$$\boldsymbol{F}_R(\boldsymbol{k}) = \boldsymbol{F}_R^{(0)} + \sum_s \boldsymbol{F}_R^{(s)} e^{iks} \tag{6}$$

where 0 indicates the starting unit cell and s ($s = -n, \ldots, -2, -1, 0, +1, +2, \ldots, +n$) is the distance of interaction between the 0th unit and the sth neighbouring units. Since we assumed that the oscillators are kinetically uncoupled, from equation (5):

$$\boldsymbol{G}_R = \boldsymbol{G}_R^{(0)} \tag{7}$$

In our model we take into account interactions in the potential only limited to the first neighbours ($s = \pm 1$) and consider only spectroscopically active $\boldsymbol{k} = 0$ phonons. Thus equations (5) and (6) reduce to:

$$\boldsymbol{G}_R(0) = \boldsymbol{G}_R^{(0)} \tag{8}$$

$$\boldsymbol{F}_R(0) = \boldsymbol{F}_R^{(0)} + \boldsymbol{F}_R^{(-1)} + \boldsymbol{F}_R^{(1)} \tag{9}$$

The model we consider here consists of an infinite array of C═O dipoles placed in an antiparallel way at a distance d (*Figure 4*). This chain contains two C═O per unit cell.

The $\boldsymbol{G}_R$ matrix takes the form:

$$\begin{array}{c|cc|cc|cc} & r_1^{(-1)} & r_2^{(-1)} & r_1^{(0)} & r_2^{(0)} & r_1^{(1)} & r_2^{(1)} \\ \hline r_1^{(0)} & & & \mu & & & \\ r_2^{(0)} & & & & \mu & & \end{array} \tag{10}$$

where $\mu = (m_C + m_O)/m_C m_O$, m_C and m_O being the masses of the C and O atoms respectively.

The $\boldsymbol{F}_R$ matrix takes the form:

$$\begin{array}{c|cc|cc|cc} & F_{r1}^{(-1)} & F_{r2}^{(-1)} & F_{r1}^{(0)} & F_{r2}^{(0)} & F_{r1}^{(1)} & F_{r2}^{(1)} \\ \hline F_{r1}^{(0)} & & f_{rr} & K & f_{rr} & & \\ F_{r2}^{(0)} & & & f_{rr} & K & f_{rr} & \end{array} \tag{11}$$

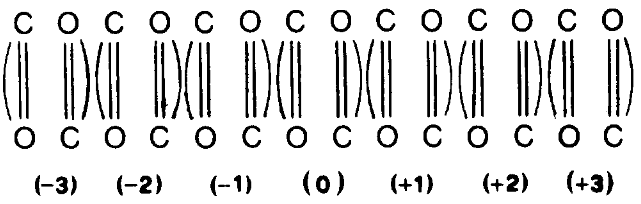

Figure 4 Model of an array of antiparallel C=O groups as an array of vibrating antiparallel dipoles

where K is the diagonal force constant and f_{rr} has been defined in equation (3).

From equation (11) one obtains:

$$F_R(0)=\begin{vmatrix} K & 2f_{rr} \\ 2f_{rr} & K \end{vmatrix} \qquad (12)$$

The resolution of the eigenvalue equation for $k=0$ gives the following eigenvalues:

$$\lambda_1 = K\mu - 2\mu f_{rr} \qquad \text{i.r.-active}$$

$$\lambda_2 = K\mu + 2\mu f_{rr} \qquad \text{Raman-active}$$

Knowledge of the numerical value of K is unnecessary since we are interested in the splitting:

$$\Delta\lambda = \lambda_1 - \lambda_2 = -4\mu f_{rr} \qquad (13)$$

For the geometry of the model chosen the expression for f_{rr} of equation (3) reduces to:

$$f_{rr} = -|\partial M/\partial r|^2/d_{\mathrm{AB}}^3 \qquad (14)$$

The use of the above model for the prediction of the splitting between in-phase and out-of-phase modes (equation (14)) requires knowledge of the dipole derivative term $|\partial M/\partial r|$, which we take from the quantum-chemical calculations on methyl acetate *in vacuo* described in an above section. One can then either assume a distance d and predict the splitting or can use the experimental splitting to measure the distance. The use of the experimental splitting for methyl acetate ($\Delta\nu = 15\ \mathrm{cm}^{-1}$) yields $d_{\mathrm{AB}} = 3.393$ Å, in very good agreement with the experimental minimum distance between C=O groups ($d_{\mathrm{AB}} = 3.92$ Å) recently measured for a polyester liquid crystal in the K phase[12]. Analogous calculations made for ethyl acetate ($\Delta\nu = 8\ \mathrm{cm}^{-1}$) give $d_{\mathrm{AB}} = 4.28$ Å. The fact that the splitting is smaller and the distance is somewhat larger may indicate that the dipoles are not fully antiparallel as predicted in the model. If dipoles were forming a helix, selection rules would be different, and A and E modes should occur with two i.r. and Raman coincidences[13]. A more detailed discussion of the vibrational spectrum of ethyl acetate is, however, outside the scope of this work.

THE CASE OF THE LIQUID-CRYSTAL POLYESTER HTH-10

As mentioned in the first section, the experimental fact that has triggered our interest in dipole–dipole splitting between C=O groups is the observation of the temperature-dependent multiplicity of bands in the C=O stretching region of the i.r. spectrum for the liquid-crystal polyester HTH-10[1]. This observation waits for some interpretation either supporting the model of dipole interactions or requiring some other justification[1].

The spectrum of the smectic and isotropic phases of HTH-10 shows two main i.r. bands at 1745 and 1724 cm^{-1} assigned to the stretchings of the 'internal' (I) and 'external' (E) C=O groups respectively within the chemical repeat unit[1]. The I groups are attached directly to the aromatic fragment, which contains the centre of symmetry.

Going to lower temperatures in the K phase each of the i.r. bands above splits into multiplets (sometimes quartets are generated for each band), whose relative intensities depend also on the thermal history during the preparation of the sample.

Since we wished to apply the model presented above also to the case of HTH-10, we made the following assumptions:

(i) The intramolecular and intermolecular geometry of HTH-10 is assumed to be similar to that of bis[(4-butoxycarbonyl)phenyl] terephthalate, recently determined from X-ray diffraction studies by Sirigu *et al.*[12]. The C=O/C=O distances between molecules and their mutual orientation were taken from ref. 12.

(ii) The equilibrium dipole moments and dipole derivatives for the C=O groups were assumed to be the same for all groups and the values were assumed to be identical to those calculated for methyl acetate.

(iii) In the calculations of the interactions we have considered separately the contributions by all possible C=O/C=O pairs (I–I, I–E, E–E) within a distance of 8–9 Å. Moreover, the mutual orientation of the dipoles was taken into account as required in equation (3).

From the calculations it turns out that only the intermolecular I–I interactions between C=O groups at short distances contribute to a sizeable splitting. The pair of C=O groups at a distance of 3.92 Å produces a calculated $\Delta\nu = 12\ \mathrm{cm}^{-1}$. The fact that only groups at short distances produce splittings is reasonable since in equation (3) the interaction potential decreases with d^{-3}. Thus any kind of sizeable dipole–dipole splitting must come from dipoles at close distances.

CONCLUSIONS

The model of dipole–dipole interactions in an array of dipoles accounts nicely for the spectroscopic observations on simple esters taken as model molecules for more complex polyester polymers. The dipole–dipole distances 'measured' with the model we propose are in remarkable agreement with the van der Waals contacts experimentally measured for molecules containing ester groups.

The dipole forces, however, die very quickly with d^{-3}, and thus only C=O groups in close contact may generate observable splitting in the infra-red and/or Raman spectra. The maximum distance capable of producing observable splitting cannot be larger than $\approx$4–5 Å.

In the case of the liquid crystal considered in this work the chemical repeat unit contains I and E ester groups. The C=O stretching frequencies of the I and E groups within each molecule are different because of the intramolecular electronic configuration[1]. (Two I C=O groups are involved in conjugation with the π electrons of the same internal benzene ring to which they are attached; only one E C=O group is instead conjugated with the external benzene ring.) If intermolecular dipole–dipole interactions were active, we would expect splitting of the stretching of the I C=O groups and not of the E C=O groups since the I C=O face each other

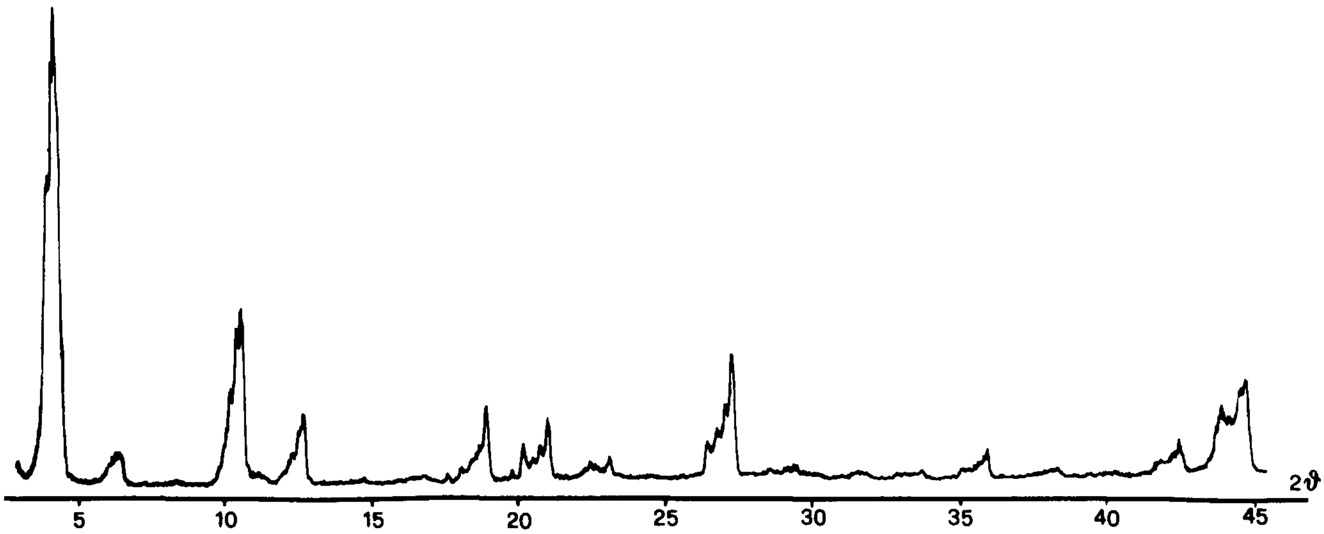

Figure 5 X-ray diffractogram of HTH-10

at closer distances. The vibrations of the E modes should not be split.

The predictions of the model, as above, are not in agreement with the observations, which do show splitting for both I and E C=O groups. Thus our hopes to find indications that dipole–dipole forces are selectively and efficiently active in HTH-10 polyester even in the K phase are not met.

In paper 1 we proposed two hypotheses for the explanation of the observed multiplet. The first suggestion was that dipole–dipole interactions were active. From this work this explanation cannot be supported. The second proposed interpretation was that the sample consists of a mixture of N unit cells similar in symmetry but with different unit-cell parameters where the environments of the I and E groups are different, probably because of slightly different chain packing due to slightly different conformational distortions. If this were the case we should expect to observe splitting in both the C=O stretching vibrations of the I and E groups, as indeed unquestionably observed.

In order to prove the existence of more than one kind of unit cell we have recorded the powder X-ray diffraction spectrum of the same material as studied with spectroscopy. The spectrum is reported in *Figure 5*. The broadening and especially the indented shape of the peaks of the diffraction pattern indicate a non-regular distribution of the values of the corresponding interplanar spacings. In particular the diffraction peak at $2\theta = 27\text{–}28°$, which is the best resolved, since it takes place at the highest angular value, clearly reveals that four different mean values of the interplanar spacing contribute to this reflection. Therefore at least one parameter, but probably also other parameters, of the unit cell exhibit four distinguishable mean values.

The most important conclusion of general relevance when spectroscopy is used as a probe is that the vibrational spectra are sensitive only to phenomena that occur at short ranges, even when highly polarizable π electrons are involved.

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