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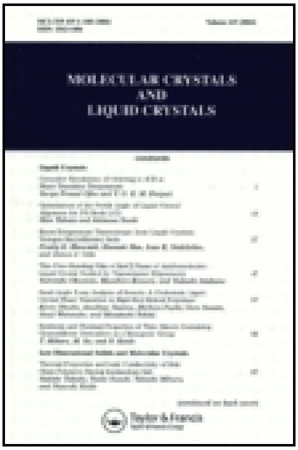

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The Phase Transition of m-Nitrophenol

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The Phase Transition of *m*-Nitrophenol

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The monocrystals of two polymorphic phases of *m*-nitrophenol were studied by the DSC method, and near IR (NIR) and far IR (FIR) spectroscopy. We found the phase transition of the first order 14 degrees below the melting point. The temperatures, enthalpies and entropies of the phase transition and the melting are presented. The polarized NIR spectra in the region of the overtones of the OH. . .O stretching vibrations for the two phases are presented. The polarized FIR spectra of the two phases in the room and liquid nitrogen temperature from 0 to 200 cm^{-1} are presented.

1. INTRODUCTION

It is known that *m*-nitrophenol exists in two polymorphic phases: monoclinic, space group $P2_1/n$ and orthorhombic, space group $P2_12_12_1$. In both phases there exists hydrogen bonding in the form of chains along the c crystallographic axis.[1] The orthorhombic phase having the noncentrosymmetric structure is probably responsible for the nonlinear optical properties revealed by *m*-nitrophenol (s.h. generation).[1,2] Up to now any phase transition of *m*-nitrophenol was not known. To the contrary, the calorimetric investigations made by means of the DSC method have not discovered any phase transition in *m*-nitrophenol from 193°K up to the melting temperature.[3] Realizing that the structures of the two phases of *m*-nitrophenol differ by their symmetries (the orthorhombic one is noncentrosymmetric) and in both there exists the hydrogen bonding, we thought it interesting to study them by spectroscopy methods. We decided also to revise the calorimetric investigations.

2. EXPERIMENTAL

m-Nitrophenol, produced by Politechnika Śląska, Gliwice, Poland, was purified by sublimation under vacuum. The final product melted at 370°K. We obtained

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the single crystals of the two phases by means of crystallization from benzene and acetone solutions. The crystals differ abruptly by their morphology. The monoclinic phase crystallizes in the form of thin plates ($10\bar{1}$). The orthorhombic one grows in the form of blocks enlongated in the direction of the crystallographic b or c axis. The monocrystals of both phases were oriented roetgenographically. We resolved also the orthorhombic structure to obtain the atomic positions needed in the calculations of dichroic ratios.[4]

The calorimetric investigations were performed using DSC-1 Perkin Elmer apparatus. We used samples weighing from 5 to 10 mgrams, the maximum range and the minimum speed of heating.

The polarized near-infrared (NIR) spectra were measured for monocrystals in the region of overtones of the OH and CH oscillators. We used the spectrophotometric assembly described earlier[5] with a Carl Zeiss SPM-2 monochromator.

The polarized far-infrared (FIR) spectra were measured for monocrystals of both phases in the 0 to 200 cm^{-1} region. The orthorhombic phase we have measured also in the liquid nitrogen temperature. We used the Fourier transform spectrometer set equipped with a cryostat. The set cooperated with a microcomputer. The Fourier transforms were calculated using the Cooley–Tukey algorithms. The resolution of measurements was about 1.5 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Calorimetry

We have examined the crystals of both phases by means of the DSC method. We have also observed them in the microscope with heated table. We have found that the orthorhombic phase exhibits a phase transition 14 degrees below the melting point. It is a first order phase transition—we have observed the phase boundary moving through the crystal. The phase transition is connected with a great hysteresis. We have not observed any reversible phase transition. The high temperature phase is a monoclinic phase known previously and remains metastable for some time at room temperature. The crystals of the monoclinic phase obtained from solution are not stable and after some time (months) become destroyed. The DSC curve is shown in Figure 1. The melting is connected with two kinds of hysteresis: when the grains of the monoclinic phase are present in the melt, the crystallization takes place 3 degrees below the melting point, i.e., at 367°K. If there are no grains of the solid state, the hysteresis is greater and the crystallization takes place at 348°K. The phase situation occurring in *m*-nitrophenol is presented in Figure 2. Table I presents the enthalpies and entropies of phase transition and melting of *m*-nitrophenol.

3.2. NIR spectroscopy

In the two phases of *m*-nitrophenol there exists hydrogen bonding in the form of chains along the crystallographic c axis. It joins molecules equivalent along the c axis. We thought it interesting to observe and compare the bands of the OH

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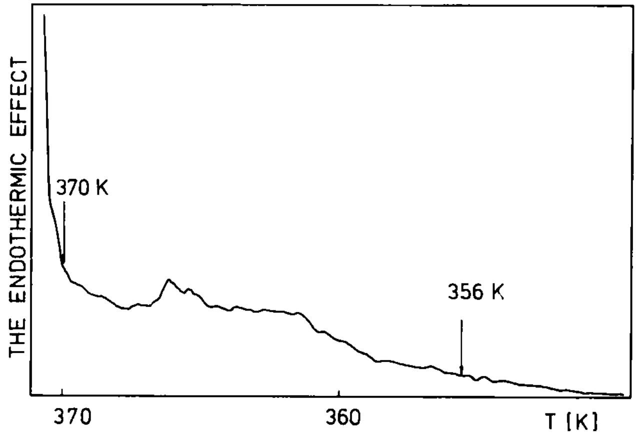


FIGURE 1 The DSC curve of the orthorhombic phase of *m*-nitrophenol.

oscillators in the crystals of both phases. Figure 3a shows the spectrum of the saturated solution of *m*-nitrophenol in CCl_4. One can see the narrow band of the free OH oscillators and the wide band of four CH oscillators in a molecule. Figure 3b shows the polarized NIR spectra of the monocrystal of the monoclinic phase of *m*-nitrophenol. The wide band between 6900 and 6300 cm^{-1} corresponds to the overtone of the stretching vibration of bonded OH groups. The sharp band at 6080 cm^{-1} corresponds to the CH stretching vibration. Figure 3c presents the NIR spectra in the same region of the monocrystals of the orthorhombic phase of *m*-nitrophenol in five different polarizations. One can see that for the polarization along the c direction the absorption is highest. It is well understood because the hydrogen bonding chains lie along the crystallographic c axis. The absorption $\parallel$ a, $\parallel$ b, $\perp$ c becomes very weak in the 6900 to 6300 cm^{-1} frequency region for the same reason in the three cases. The absorption band corresponding to the polarization along the [101] direction is comparable to the same band for the monoclinic phase (Figure 3b), which agrees with roetgenographic results.[1,4]

We tried to compare the experimental and theoretical dichroic ratios, calculated according to the oriented gas-model method described in Reference 6. It was possible to compare only the intensities of the bands corresponding to the polarizations along the c and [101] directions. All the bands in other polarizations ought to have zero intensities. Unfortunately these two bands were measured for different crystals. Nevertheless, taking into account that the CH bands have comparable

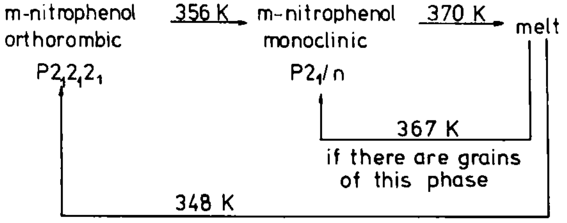
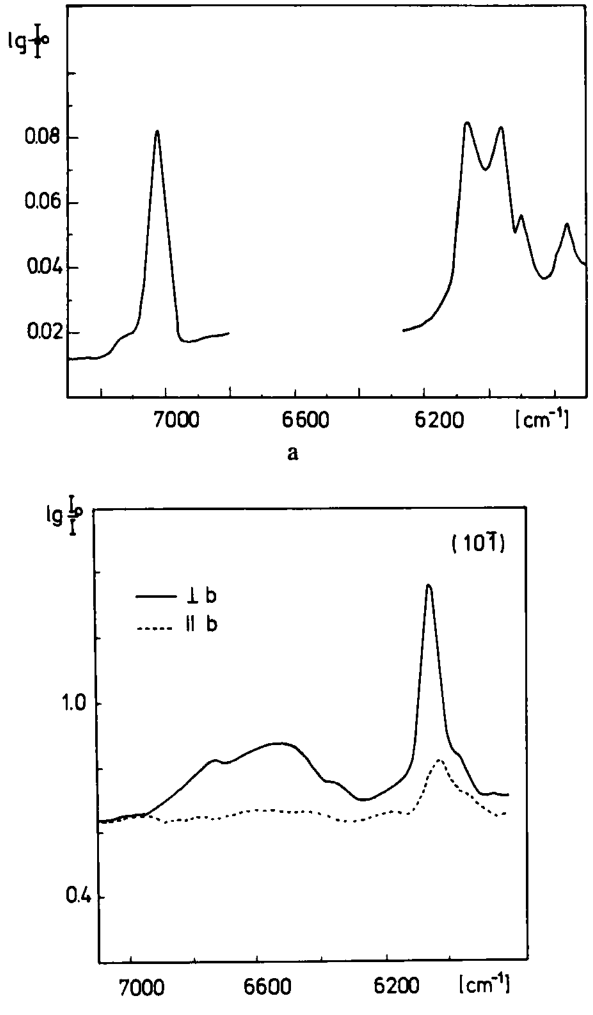


FIGURE 2 The phase situation in *m*-nitrophenol.

TABLE I

The temperatures, enthalpies and entropies of the phase transition and the melting of *m*-nitrophenol.

	Temperature	ΔH	ΔS
	K	J/mol	J/mol K
Phase transition	356	~167	~0, 47
melting	370	19,960 ± 1750	54 ± 5



b

FIGURE 3 (a) The NIR spectrum of the CCl_4 saturated solution of *m*-nitrophenol. (b) The polarized NIR spectra of the monoclinic phase of *m*-nitrophenol. (c) The polarized NIR spectra of the orthorhombic phase of *m*-nitrophenol.

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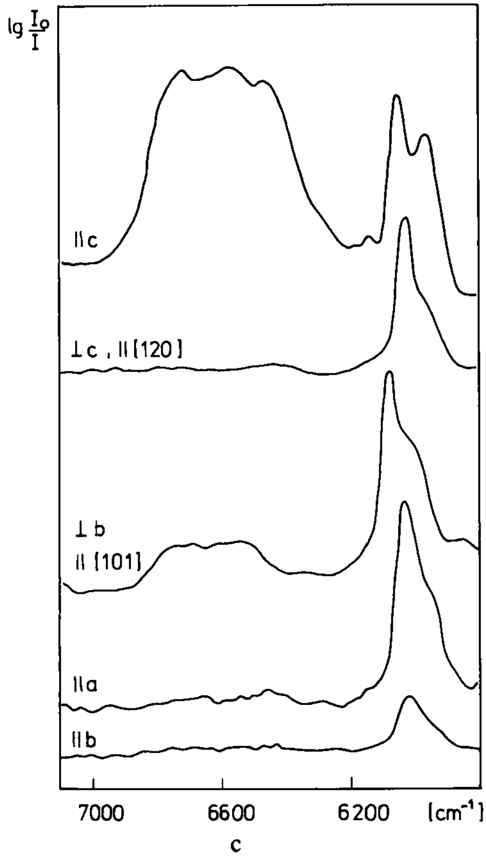

FIGURE 3 (*continued*)

intensities for the two crystals in the two polarizations, we decided to calculate the theoretical dichroic ratio for the OH. . .O band for the polarization along the c and [101] directions. The theoretical dichroic ratio $R_{[101]/c} = 0.34$. We calculated it, abandoning the ratio of refractive indices which are not known for these directions, but according to Reference 7 they ought not influence greatly the value of R. The experimental value of dichroic ratio $R_{[101]/c} = 0.19 \pm 0.01$. The discrepancy may be understood on the basis of arguments presented in Reference 8. According to them crystals revealing nonlinear optical properties (and this is the case of the orthorhombic phase of *m*-nitrophenol) cannot be treated by the oriented-gas model. We plan to check this by measuring the monoclinic phase crystal (non-electrooptic) in analogous polarizations. Nevertheless, the presented NIR spectra are in accordance with the structural results concerning the hydrogen bondings in the two phases of *m*-nitrophenol.

3.3. FIR spectroscopy

We have measured the polarized FIR spectra of the two phases in room temperature and those of the orthorhombic phase also in the liquid nitrogen temperature. Figures

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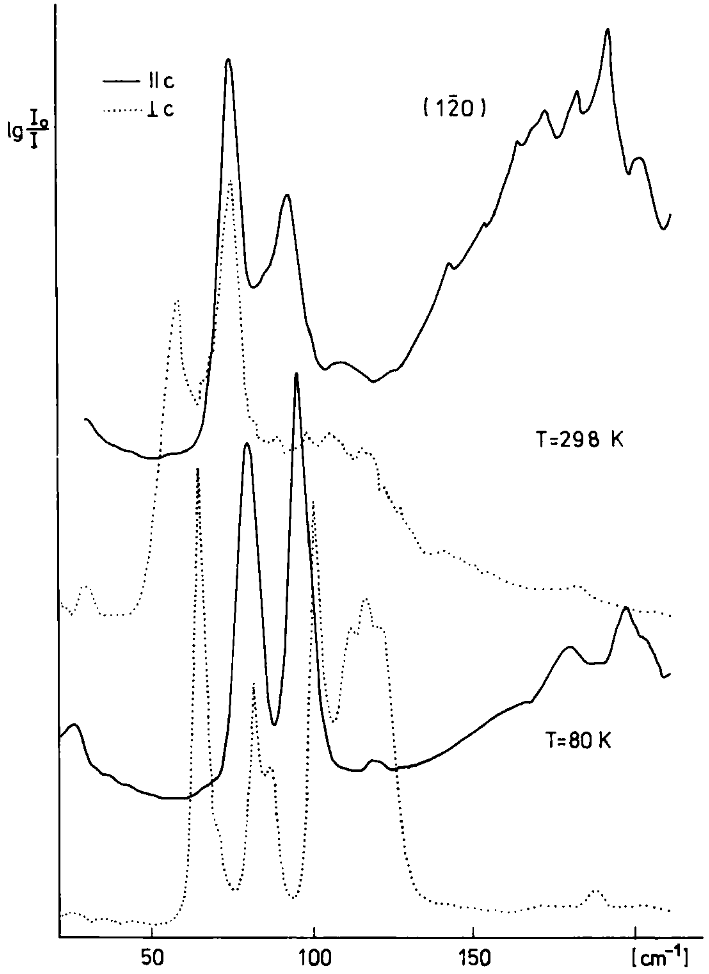

FIGURE 4 The polarized FIR spectra of the orthorhombic *m*-nitrophenol monocrystal.

4 and 5 present the spectra for the orthorhombic and monoclinic phase, respectively. The measured frequencies of lattice vibrations and their symmetries resulting from the group theory analysis according to Sanquer[9] are given in Table II.

The conditions given by the group theory concerning the number of active vibrations seem to be fulfilled for both phases. The values of lattice frequencies agree with corresponding values found in similar compounds, e.g., *m*-nitroaniline,[10] *m*-aminophenol,[11] and *m*-chloronitrobenzene.[12] In spite of the different crystal structure of *m*-nitrophenol this is probably due to the similar intermolecular interactions in this type of compound. The values of the lattice frequencies for both phases of *m*-nitrophenol are almost the same. This is caused by the fact that the positions of atoms in both structures are very similar, hence the energy of mutual interaction does not differ much. The principal difference between the two phases

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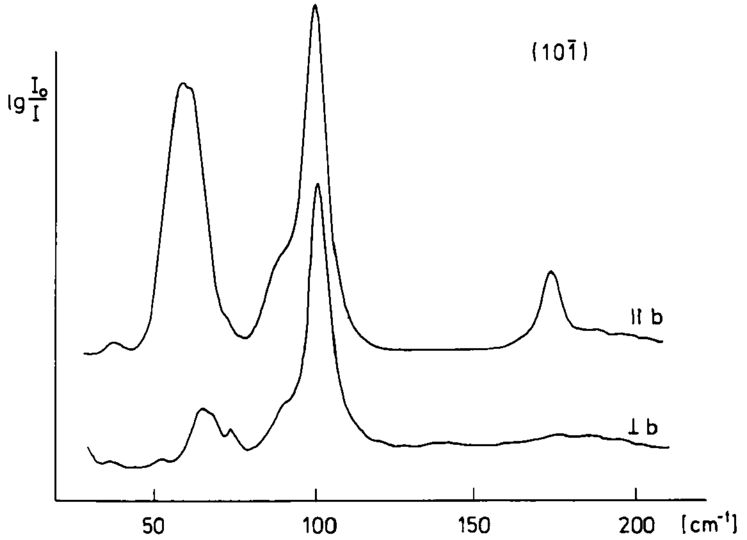

FIGURE 5 The polarized FIR spectra of the monoclinic *m*-nitrophenol monocrystal.

consists of the difference in the symmetries (the presence or the absence of the center of symmetry) and this is very obvious in the presented spectra.

In the FIR spectra one can also see the wide band corresponding to the vibration of hydrogen bonding. It lies between 150 and 210 cm^{-1} for the polarization along the c axis in the spectrum of the orthorhombic phase. The intensities and polarizations of the bands agree with the corresponding values for the bands of the OH. . .O vibrations in the NIR region (Figure 3).

4. CONCLUSIONS

The phase transition in *m*-nitrophenol is of the first order, nevertheless it is a very subtle one. The enthalpy and entropy of it are rather small. The two polymorphic

TABLE II

Symmetry of crystal	Polarization	Frequency	Symmetry of vibration	Comments
$P2_12_12_1$ $Z = 4$	E ∥ c	76,78,82,94,118	$5B_1$	T ≅ 80 K
	E ⊥ c	36,45,63,64,80 85,99,110,114,119	$5B_2 + 5B_3$	
$P2_1/n$ $Z = 4$	E ⊥ b	65,75,92,101	$4B_u$	The low resolution of the last three bands T ≅ 298 K
	E ∥ b	56,60,65,91,101	$5A_u$	

phases differ strongly by their crystal symmetries but very little by the positions of atoms. In addition in both phases there exists the hydrogen bonding, joining the equivalent molecules along the crystallographic c axis. The space groups of both phases are $P2_12_12_1$ and $P2_1/n$. The main difference between the two structures consists in the reflection of half of the molecules in the [001] plane. It is rather difficult to imagine that in the temperature of the phase transition half of the molecules lying almost on the [a, c] plane break the hydrogen bondings, make a jump of 180° and reconstruct practically the same hydrogen bondings. We think rather that the phase transition path leads through some "intermediate state." This process may require some activation energy. $P2_12_12_1$ and $P2_1/n$ space groups have no common point group. Perhaps the symmetry of the "intermediate" phase joins the symmetries of the two known phases of *m*-nitrophenol, e.g., it might be $P2_1$. Of course these are only speculations, but we plan to check them by studying the spectra of the orthorhombic phase in function of temperature.

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