

## SPECTROSCOPY INVESTIGATIONS OF THE POLYMORPHISM OF THE SOLID PHASE OF MBBA\*\*\*

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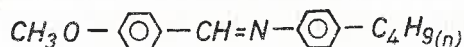
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Liquid crystals often form not one but several solid phases: N-p-[(methoxybenzylidene)-p'-butyl] aniline (MBBA) has three phases: one glasslike and two crystalline phases: one metastable and one stable. IR absorption spectroscopy was applied to investigate the solid phase polymorphism and phase transformation between different phases in this substance.

### 1. Introduction

In recent years, apart from the extensive continuation of research on the structure and properties of liquid-crystalline phases, a new branch of research on mesomorphic molecules has developed: studies of solid phases of these compounds. These investigations have led to the discovery of polymorphism of the solid phase in several liquid-crystalline substances which after melting form smectic, nematic or cholesteric [1-6]. Polymorphism has been very thoroughly investigated for the compound N-[p-(methoxy-benzylidene)-p'-butyl]-aniline (MBBA) [7-14] which has the following formula:



This compound forms three solid phases: glassy (at rapid cooling), and two crystalline phases, a metastable and stable one. The metastable phase transfers spontaneously and irreversibly to the stable one [7, 8, 14].

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A brief presentation of IR spectra of both crystalline modifications of MBBA was given in the previous work [8]. Lately Destrade and Gasparoux presented a detailed Raman study of solid phase polymorphism for this substance [11]. Therefore it is natural to present here a more detailed analysis of the IR spectra of both crystalline modifications of MBBA as a study complementary to paper [11]. The attempt to study the metastable to stable phase transformation by spectroscopy will also be discussed here and compared to the calorimetric results [14].

## 2. Experimental

In all measurements a spectroscopically pure sample supplied by Riedel de Haën AG Seelze-Hannover, was used.

Measurements of the absorption spectra of MBBA were performed using Zeiss UR-10, UR-20 and Unicam SP 1200 spectrophotometers in the wave number range  $400\text{ cm}^{-1}$  to  $3600\text{ cm}^{-1}$  and temperature range 80 K to 320 K. The resolutions of the apparatus were  $3\text{ cm}^{-1}$  and  $1\text{ cm}^{-1}$ , respectively. The sample had the shape of a thin layer between two AgCl plates, situated in a cryostat. The accuracy of the temperature measurements was  $\pm 1\text{ K}$ .

## 3. Results and discussion. Differences between crystalline modifications of MBBA

Fig. 1 presents for two temperatures the spectra of the two crystalline modifications of MBBA. The wave numbers covered are  $450\text{--}700\text{ cm}^{-1}$ . In the metastable modification three absorption bands are seen, as compared to only two for the stable modification. The band at  $545\text{ cm}^{-1}$ , which disappears at transition, probably corresponds to a C-H-rocking vibration [15].

The following part of the spectrum is presented in Fig. 2. The most striking differences occur in the region  $810\text{--}870\text{ cm}^{-1}$  in which for the metastable modification 5 intense bands appear, whereas only one band at  $840\text{ cm}^{-1}$  is seen for the stable modification. On the basis of an analysis of the vibrations of n-butyl fluoride made by Crowder and Mao [16], we may think that one band in the stable phase is connected with C-H-rocking vibration in the butyl group in the "trans" conformation, whereas the close-lying vibrations in the metastable form could correspond to the "gauche" conformations of n-butyl. Unfortunately, these assignments are not certain as these could also be vibrations connected with the benzylideneaniline core, as for the pure benzylideneaniline Vergoten and Fleury [17] obtained vibrations in this frequency range. Differences also occur for that part of the spectrum from  $1000$  to  $1300\text{ cm}^{-1}$ , which is presented in Fig. 3. Here the band at  $1030\text{ cm}^{-1}$  (O-CH<sub>3</sub>-stretching) single in the metastable form splits into two vibrations in the stable phase. Bands occurring at about  $1100\text{ cm}^{-1}$  which may be connected with C-OCH<sub>3</sub>- and CH<sub>3</sub>-rocking vibrations or with a combination of deformations of the benzene ring [17], also reflect the differences between the two forms.

The presented spectra provide multiple evidence for a statement that both modifications of MBBA differ not only in the arrangement of molecules in the crystal lattice but also

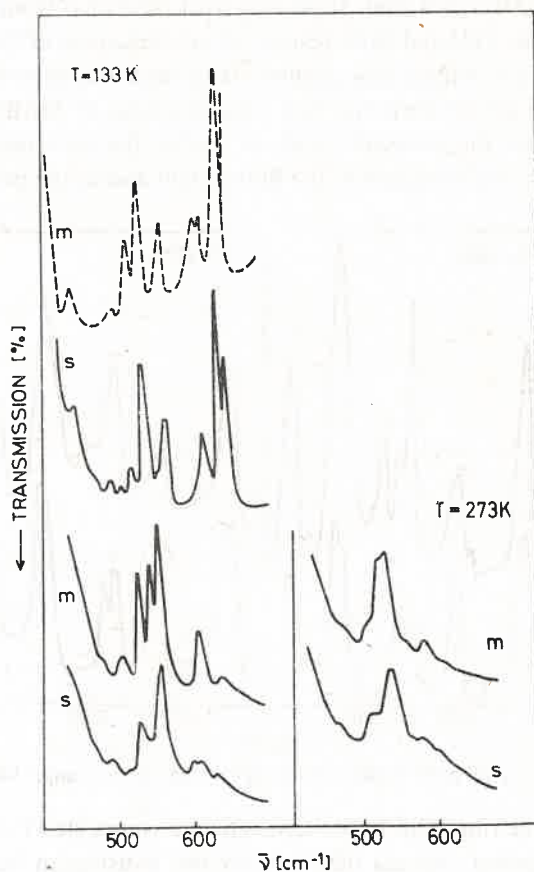


Fig. 1. Spectra of both modifications of MBBA in the range  $400\text{--}700\text{ cm}^{-1}$ . Two upper curves — Raman spectra of metastable (broken) and stable (full) modifications [11]. The lower spectra — these IR results

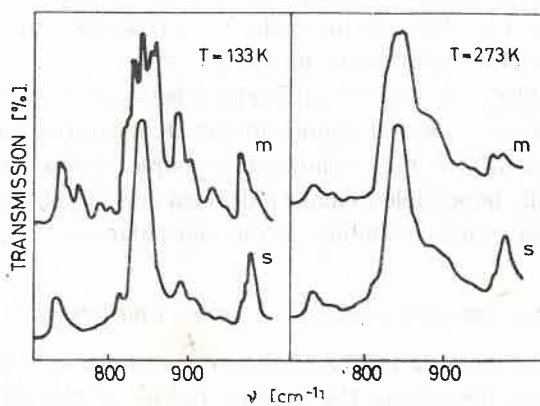


Fig. 2. IR spectra of both modifications of MBBA in the range  $700\text{--}1000\text{ cm}^{-1}$

in molecular structure. It seems that, from this work and also from the Raman study of Destrade and Gasparoux [11] and from results of investigations of the dielectric relaxation by Mościcki [18], one can supply new arguments to back the hypothesis of Andrews [19] concerning the difference between the two modifications of MBBA. According to this hypothesis, the shape of the molecular body is similar for both modifications, but there occur differences in the conformation of the butyl chain and in the position of the methoxy

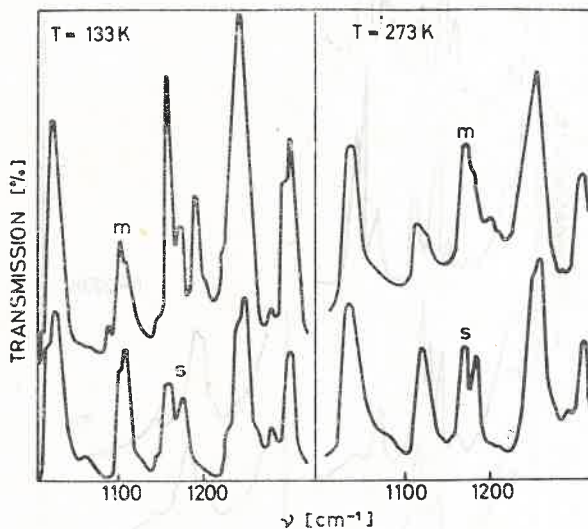


Fig. 3. IR spectra of both modifications of MBBA in the range 1000—1300  $\text{cm}^{-1}$

group with respect to the ring. This hypothesis is further supported by the fact that in EBBA (in which an ethoxy group replaces the methoxy one causing an increase of the number of possible conformations) Ogorodnik has lately found a few metastable phases [4]. The conclusions of Ogorodnik [4] based upon the differences in Raman spectra in 1150—1200  $\text{cm}^{-1}$  for different phases of EBBA. Our IR spectra of MBBA are also different in the same region for the two solid modifications. These results for EBBA were confirmed recently by Cavatorta et al. [21] for the region 10—1650  $\text{cm}^{-1}$  by Raman spectroscopy measurements and by DSC calorimetry method.

It should be pointed out that the differences between the two modifications for MBBA appears in the same spectral regions in our IR measurements and in the Raman measurements reported in [11]. Fig. 1 shows an example of this similarity of behaviour. It is of course practically impossible to make a detailed analysis of the two kinds of spectra and hence to get a clearer understanding on the molecular level.

#### 4. A proposal for studying the metastable $\rightarrow$ stable transformation by the IR method

In our attempts to measure the kinetics of the metastable  $\rightarrow$  stable transformation particular attention was devoted to the thermal history of the sample. All procedures started by melting the sample to the nematic phase, after which a rather rapid cooling

to the chosen "residence" temperature  $T_r$  followed. In this manner we were always obtaining the metastable modification. This modification was then kept at this temperature for a given time,  $t_r$ . Two "residence times" were used: a long one of about 8 hours and a short one of about 1 hour. After that time the temperature was raised to the chosen value of  $T_p = 275$  K

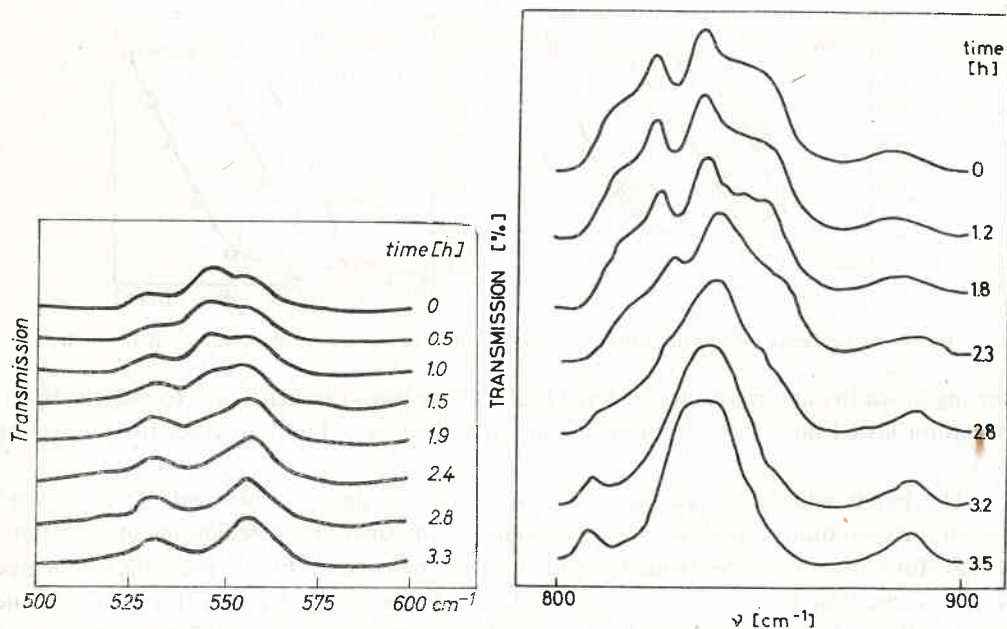


Fig. 4. Changes in the MBBA spectrum during phase transformation; (1) — range 500–600  $\text{cm}^{-1}$ , (b) — 800–900  $\text{cm}^{-1}$

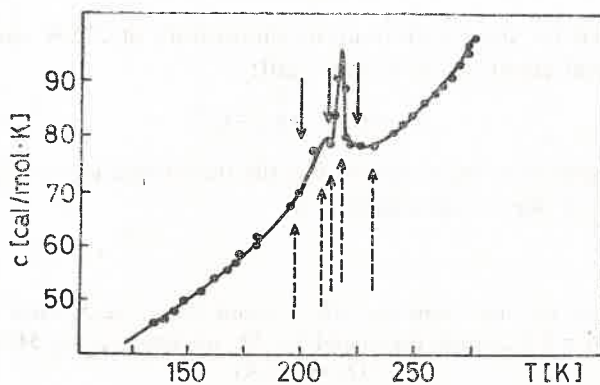


Fig. 5. Temperatures to which the metastable modification of MBBA was cooled ( $T_r$ ) compared with the curve of specific heat,  $C_p$ , of that variety. Full arrows —  $t_r = 8$  h, broken arrows —  $t_r = 1$  h

and the spectrum was measured for the range 450  $\text{cm}^{-1}$  to 1300  $\text{cm}^{-1}$ . Time evolutions of the spectrum in the 500–600  $\text{cm}^{-1}$  range (a) and 800–900  $\text{cm}^{-1}$  range (b) are presented in Fig. 4. In Fig. 5 taken from [7], the curve of the specific heat of the metastable modification of MBBA is presented; arrows mark the residence temperatures  $T_r$  of the metastable

sample (full arrows correspond to the longer residence time,  $t_r = 8$  h, and broken ones to  $t_r = 1$  h). It should be pointed out that the metastable to stable transformation of a sample cooled from the nematic phase directly to 285 K without an additional lowering of temperature to the residence temperature  $T_r$  was also observed. In this case a significant

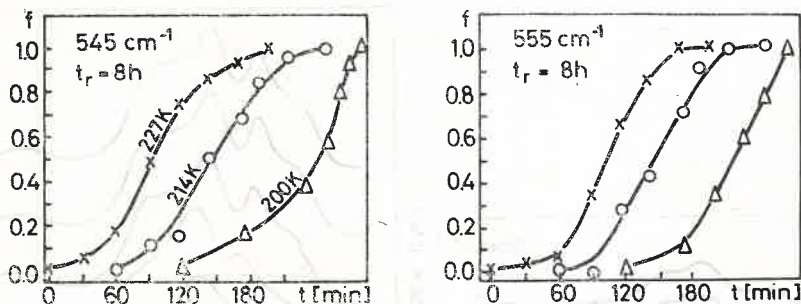


Fig. 6. Dependence of  $f(t)$  for  $545\text{ cm}^{-1}$  and  $555\text{ cm}^{-1}$  bands for three  $T_r$  values at  $t_r = 8$  h

slowing down (by about a factor of four) in the phase transformation was found, the transformation lasted now about 15 hours as compared to ca. 4 hours in cases for precooling to  $T_r$ .

The bands which showed the strong variation i.e. those at  $545$  and  $555\text{ cm}^{-1}$  were chosen for quantitative analysis. Using formula (2) of paper [14] calculations of the degree of transformation were performed for all measurement runs. Fig. 6 presents the degree of transformation i.e.  $f(t)$  dependences calculated according to that formula for the wave numbers:  $545\text{ cm}^{-1}$  (a) and  $555\text{ cm}^{-1}$  (b). Each curve represents a different temperature  $T_r$ , temperature values being written beside the curves. All curves correspond to one period  $t_r = 8$  h.

Results obtained for the transformation temperature of 275 K can be explained by the phenomenological equation of Avrami [20]:

$$1 - f(t) = \exp(-kt^n), \quad (1)$$

where  $f(t)$  is the degree of transformation,  $k$  is the transformation rate constant,  $t$  is time, and  $n$  is the order of the transformation.

TABLE I

Order of transformation ( $n$ ), transformation rate constant ( $k$ ) and normalized rate constant ( $\sqrt[n]{k}$ ), depending on  $T_r$  for  $t_r = 8$  h. Values determined by IR spectroscopy for  $545$  and  $555\text{ cm}^{-1}$  bands ( $T_p = 275\text{ K}$ )

$T_r$ [K]	Total time of transformation [h]	$545\text{ cm}^{-1}$			$555\text{ cm}^{-1}$		
		$n$	$k$	$\sqrt[n]{k}$	$n$	$k$	$\sqrt[n]{k}$
200	3.25	2.70	0.0858	0.4008	3.18	0.0351	0.3488
214	3.08	2.84	0.2332	0.5993	2.34	0.3369	0.6283
227	3.53	2.73	0.2137	0.5682	4.20	0.0631	0.5180

The obtained values of  $n$  and  $k$  and the normalized rate constant  $\sqrt[n]{k}$ , are collected in Table I.

The situation is different for the short residence period,  $t_r = 1$  h. It may be clearly seen from Fig. 7 that the transformations not start immediately. On the contrary over a certain period, the degree of transformation does not change and only begins to increase

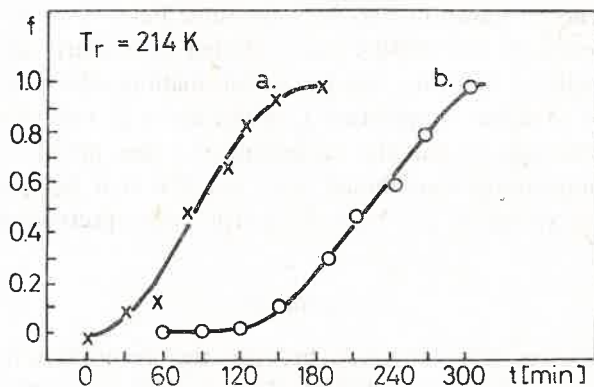


Fig. 7. Degree of transformation versus period of cooling,  $t_r$ , for one temperature of cooling  $T_r = 214$ K;  $a - t_r = 8$  h,  $b - t_r = 1$  h

after about 2—2.5 hours. The Avrami model [20] assumes that transition occurs through a competition between two processes: that of nucleation and that of propagation of the new phase. In the first stage the rate is controlled by nucleation and later the propagation plays a more decisive role. The fact that no visible changes of the MBBA spectrum are

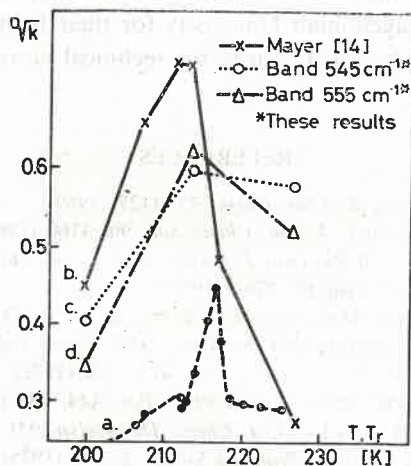


Fig. 8. Comparison of values of  $\sqrt[n]{k}$  as a function of  $T_r$ , taken from calorimetric and spectrometric measurements. The specific heat of the metastable MBBA modification in these temperatures is also shown:  $a$  — specific heat vs temperature;  $b$  —  $\sqrt[n]{k}$  vs  $T_r$  from calorimetric data [7];  $c$  —  $\sqrt[n]{k}$  vs  $T_r$  from spectroscopic data at  $545\text{ cm}^{-1}$ ;  $d$  —  $\sqrt[n]{k}$  vs  $T_r$  from spectroscopic data at  $555\text{ cm}^{-1}$

seen during the transformation observed after a short residence period ( $t_r = 1$  h) in the residence temperature  $t_r$  indicates that the nucleation processes is not completed.

For the long period,  $t_r = 8$  h in the small MBBA sample used in IR spectroscopy, complete nucleation takes place. Comparison of normalized transformation rates  $\sqrt[n]{k}$  indicates the similar character of variations depending on the temperature  $T_r$  for both methods of measurements, that is the calorimetry used in [14] and IR study made in this paper. This dependence is shown in Fig. 8. In the same figure the curve for specific heat of the metastable modification of MBBA is also plotted. It is clearly seen from Fig. 8 that the value of the normalized transition rate for transformations observed after prior cooling of the sample to the residence temperature  $T_r$  in the region of heat anomaly, reaches the maximum value. This suggests that the nucleation of a new modification is most rapid in that range of temperatures. One should point out that it is not possible to compare directly the absolute values of  $\sqrt[n]{k}$  for calorimetric with spectroscopic measurements.

### 5. Conclusions

Significant differences were observed between the absorption infrared spectra of metastable and stable modifications of MBBA. They could be connected with an existence of several "gauche" conformations of a butyl chain and methoxy group in the metastable modification of MBBA. We suspect that only one conformation exists in stable MBBA. Although Destrade and Gasparoux [11] suggested a mixture of different conformers only in the glasslike state, it is very probable that such a mixture exists also in the metastable solid phase of MBBA.

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