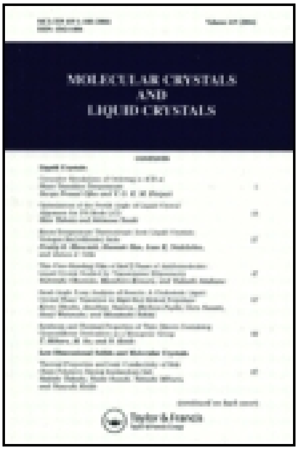

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Absorption Spectra of p-Methoxy Benzylidene p-n-Butylaniline in the 80-400 cm^{-1} Range at Temperatures Between -200 and 70°C

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Absorption Spectra of p-Methoxy Benzylidene p-n-Butylaniline in the 80-400 cm^{-1} Range at Temperatures Between -200 and 70°C

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(Received September 21, 1973)

The absorption coefficient of all phases of p-methoxy benzylidene p-n-butylaniline was measured in the 80 to 400 cm^{-1} range. An analysics of the obtained data is given. There is evidence that there are two modifications (metastable and stable) in the solid phase featuring different absorption spectra. Pretransition effects were observed to accompany all phase transitions.

INTRODUCTION

This paper presents experimental data on the temperature dependence of the absorption coefficient of liquid-crystalline p-methoxy benzylidene p-n-butylaniline (henceforth referred to as MBBA) in the infra-red range from 80-400 $cm.^{-1}$ Earlier calorimetric[1] and infra-red absorption[2] studies revealed the existence of two crystal modifications of this compound and the results of measurements in the far infrared presented here support this conclusion.

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EXPERIMENTAL

Absorption measurements were carried out in the 80 to 400 cm^{-1} range on an IRIS Fourier transform spectrophotometer (manuf. Grubb Parssons) with a Michelson interferometer. In the succesive series of measurements use was made of vessels with silicon or rigidex windows. A cryostat-thermostat allowed the samples to be examined in the temperature range from -200°C to +70°C. Sample temperature was measured with a copper-constantan thermocouple to an accuracy of ±1° C. At a resolution of 4 cm^{-1} each measurement lasted 10 min., whereas at a resolution of 2 cm^{-1} the time of measurement was 20 min. The spectra were found from the interference patters by means of an ODRA-1204 computer.

RESULTS OF MEASUREMENTS

The shape of the absorption spectra of crystalline MBBA depends on the thermal processing that any sample undergoes prior to measurement [1,2]. As has been ascertained there are two different crystal modifications of MBBA - metastable and stable. The former was obtained by freezing the nematic phase of MBBA,

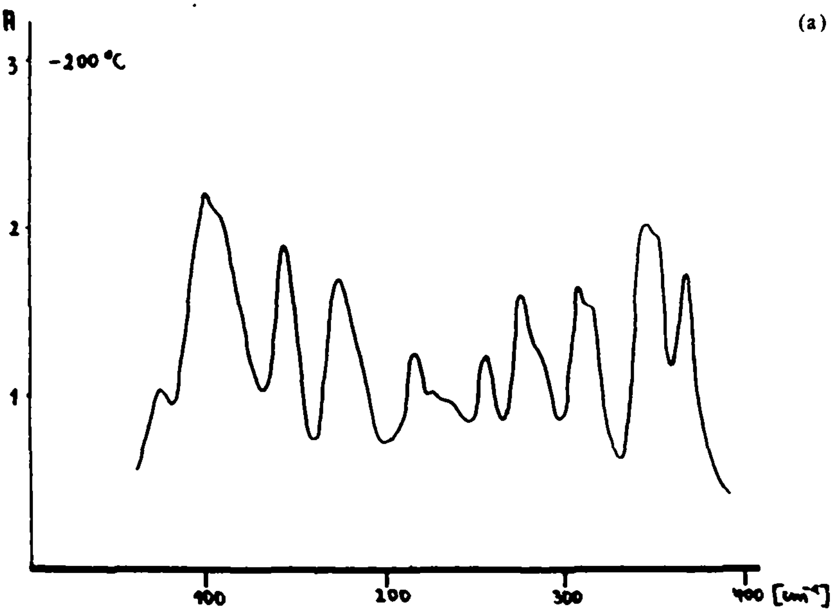
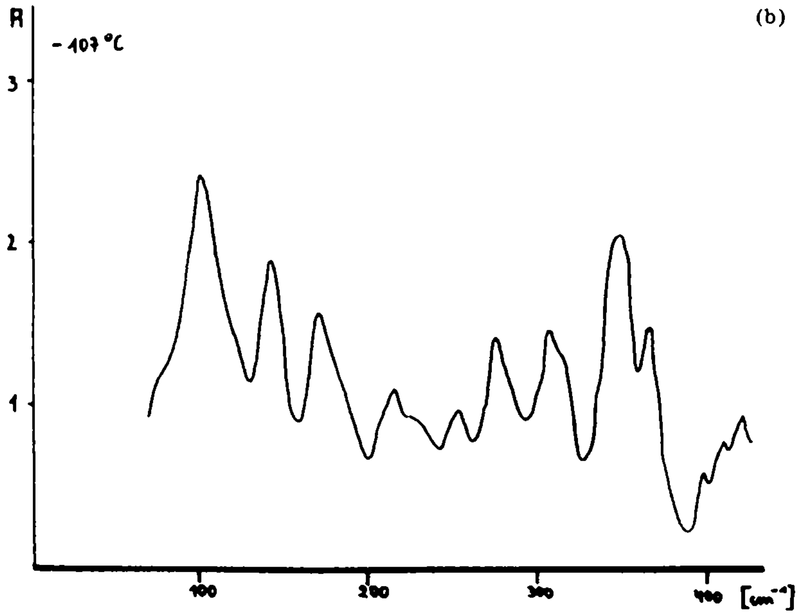
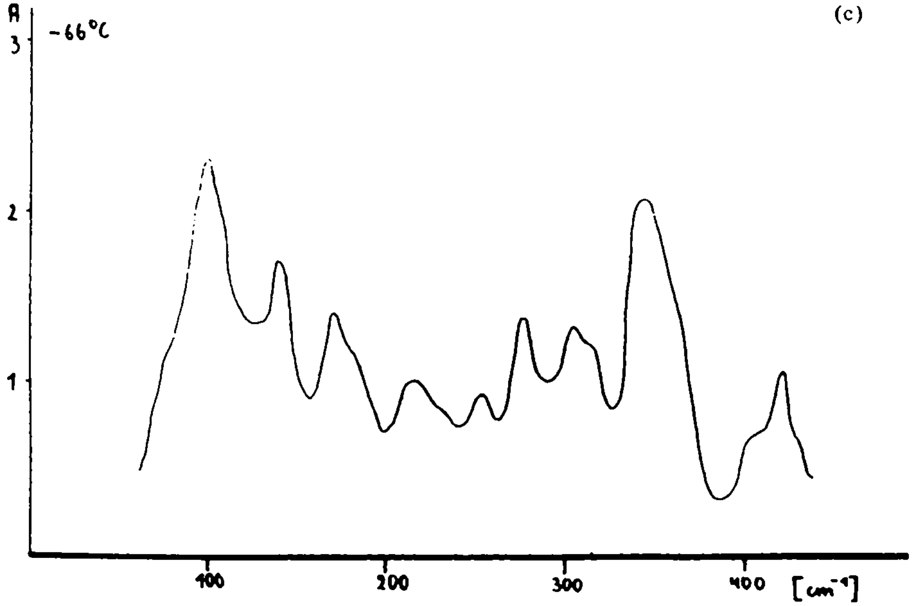
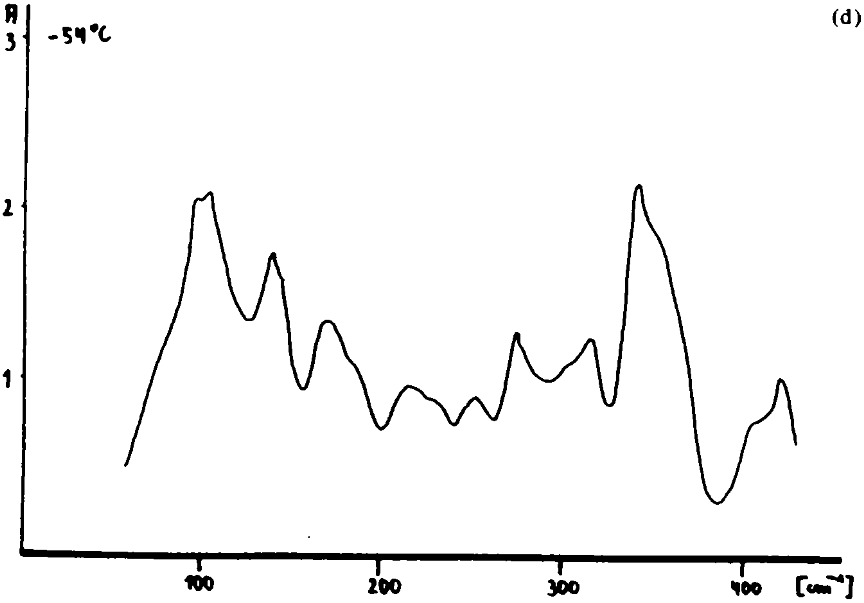
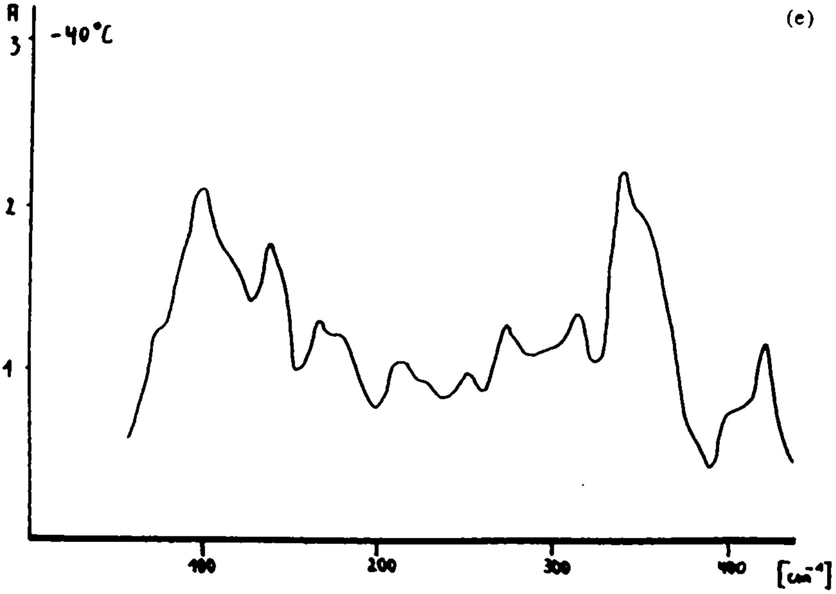


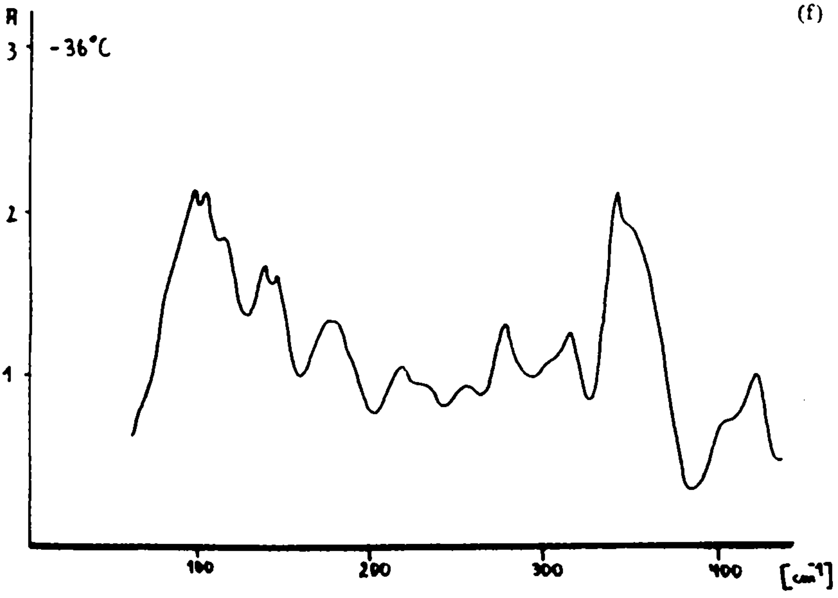
FIGURE 1 Absorption spectra of the metastable form of MBBA at the temperature: a. −200°C, b. −107°C, c. −66°C, d. −54°C, e. −40°C, and f. −36°C.


(b)
A
-107 °C
3
2
1
100
200
300
400
[cm-1]


(c)
A
-66°C
3
2
1
100
200
300
400
[cm-1]


(d)
A
3
2
1
-54°C
100
200
300
400
[cm⁻¹]


(e)
A
3
2
1
-40°C
100
200
300
400
[cm⁻¹]



while the stable form was acquired after freezing the metastable modification to liquid nitrogen temperature, then heating the substance to +16°C and maintaining it at this temperature for several hours. It must be emphasized that when the metastable form was not pre-cooled to a low temperature (in our case that of liquid nitrogen) no transition at all was observed. Experiments have also shown that the rate at which the metastable form changes into the stable one is faster when the transition point is higher.

Figure 1 shows the absorption spectra of the metastable modification at six temperatures. These spectra feature well-defined absorption bands, whose positions are entirely indepent of temperature and whose intensities are only slightly temperature dependent. Calorimetric measurements[1] demonstrate that at approx. −50°C the metastable modification undergoes some sort of phase transition. The absorption spectra (Figure 1) below and above this temperature are identical but in its immediate vicinity there is an apparent rise in absorption caused by radiation scattering.

Figure 2 presents the absorption spectra of the stable form of MBBA. These differ from the former, especially in the 100 to 150 cm^{-1} region. Instead of the two well-defined peaks at 102 and 137 cm^{-1}, there is here a broad band with a maximum at 137 cm^{-1} having a distinct structure. The temperature – dependence of the spectrum is very weak, just as was the case for the metastable modification. Just before the melting point is reached there is an almost twofold apparent rise in absorption; this effect is presumably due to the existence of

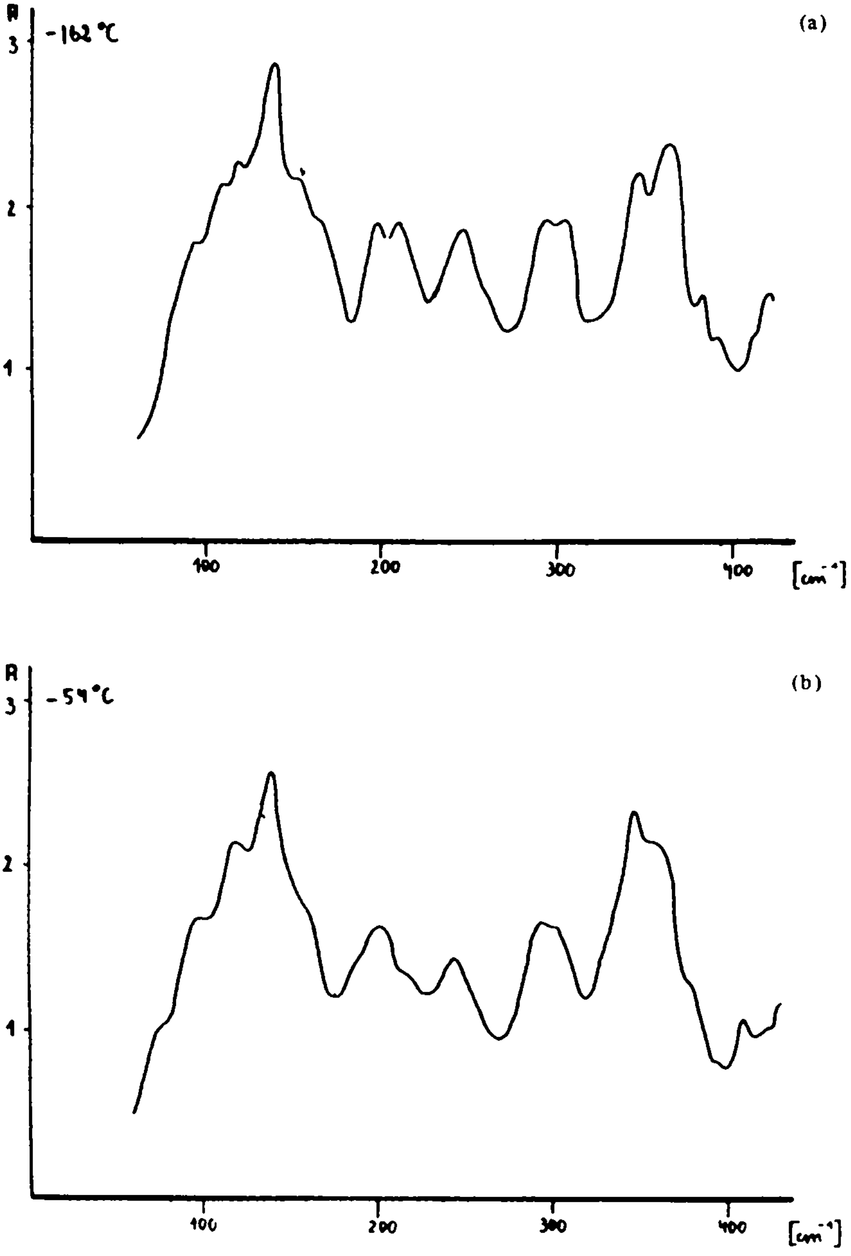
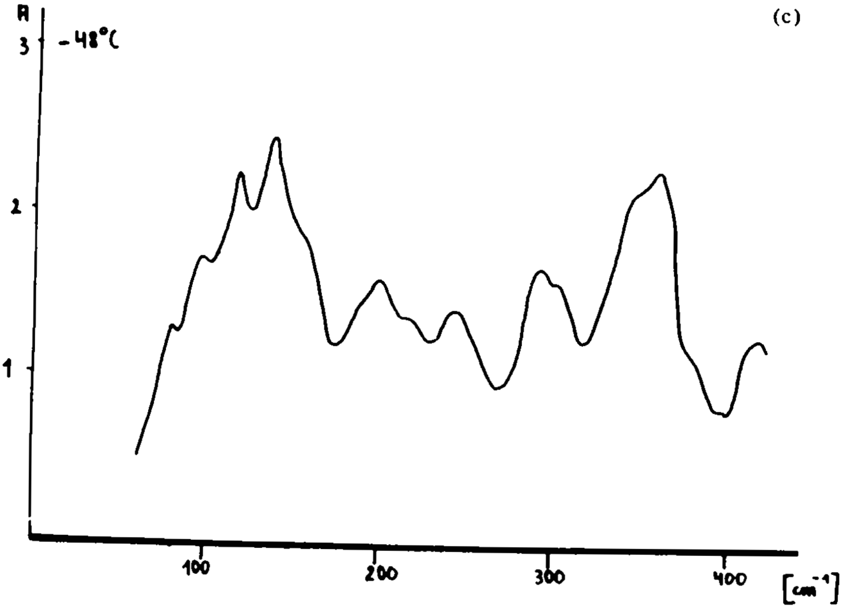
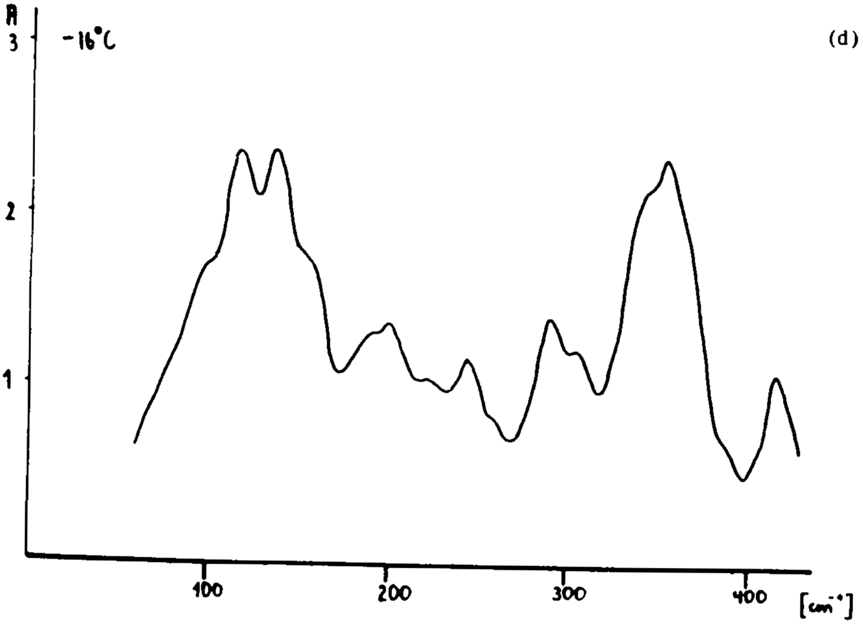


FIGURE 2 Absorption spectra of the stable form of solid MBBA at the temperatures: a. −162°C, b. −54°C, c. −48°C, and d. −16°C.


(c)
A
3
2
1
-48°C
100
200
300
400
[cm⁻¹]


(d)
A
3
2
1
-16°C
100
200
300
400
[cm⁻¹]

pre-transition processes. Figure 3 gives, by way of illustration, the absorption spectrum of the stable modification in the pre-transition temperature region. A similar effect also occurs at the melting point of the metastable MBBA.

After melting at 22°C an identical spectrum of the nematic phase is always obtained, no matter which crystal phase was fused (Figure 4). At a temperature near the transition from the nematic phase to the liquid phase at 41°C a new apparent rise in absorption is observed, again within a narrow temperature region (about 2°C).

Figure 5 shows the absorption spectrum of the isotropic liquid. The spectra of the isotropic and nematic phases of MBBA are similar to each other. It is remarkable that they also closely resemble the spectra of the stable form of MBBA. When a sample is cooled the nematic phase can be supercooled by several °C.

Table 1 presents the measured frequencies of the vibrational modes of all MBBA modifications together with their suggested interpretation.

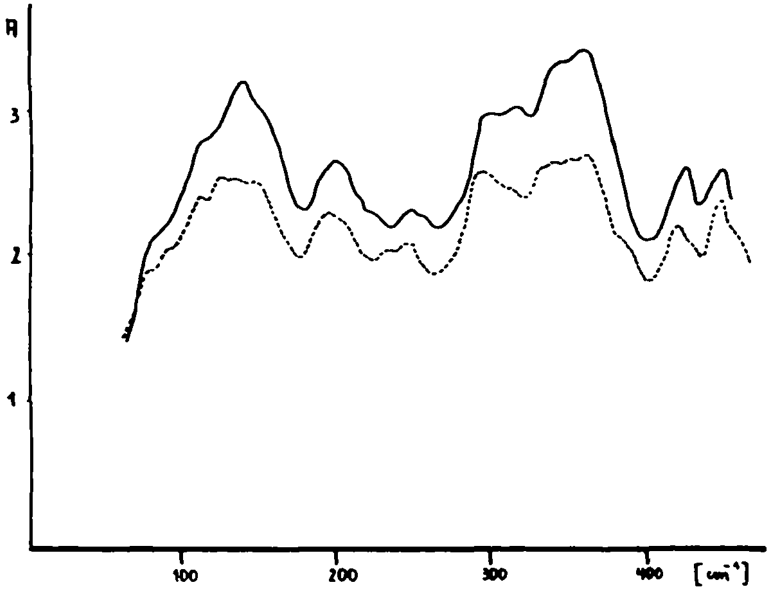


FIGURE 3 Absorption spectrum of the stable form of MBBA in the pre-transition region at 21°C (the broken line is at 19°).

TABLE I

Vibration frequencies of the MBBA modifications, in cm^{-1}, and proposed assignments

crystal-124°C stab.	crystal-127°C metastab.	nematic + 35°C	izotropic + 50°C	tentative assignment
94	94 s	90 sh w		
102 m	102 s			
117 s	117 sh			lib. C_6H_4
		129 w		
137 s	137 m	135 s		or
150 sh s	-	135 s		Lib. OCH_3
160 sh m	170 m			
	177 sh			
191 m	-	191 vw		
210 m	210 w	210 vw	210 vw	
-	225 w			tors. CH_3
242 m	-	242 vw		
253 sh w	250 w			
-	273 m			
		278 sh vw		
290 m	- _			def. C_4H_9
302 m	302 m			
	312 m	312 w		
	340 s			
344 s	347 s	344 vs		lib. CHN
360 s	360 m	360 sh s	360	
380 sh w	380 sh vw	-	-	

Notation: s - strong, m - medium, w - weak, vw - very weak (intensity), sh - shoulder, "-" - no peak.

DISCUSSION

The lack of X-ray diffraction data renders interpretation very difficult and any estimation of the frequencies of the molecule's vibrational modes even more so. Therefore, we considered four possible models of the MBBA molecule (Figure 6). The spacing between atoms and the angles between the bonds assumed for the MBBA molecule are primarily based on X-ray diffraction analyses of PAA[3]. The models presented here differ in the position and shape of the C_4H_9 branch. There are data[4] which give preference to models B and B'as being the most probable ones. The moments of inertia relative to the principal axes a, b, c, (a is the longest axis of the molecule) were calculated for all of these models. They are given in Table 2. Additionally, Table 3 gives the moments of inertia of the C_6H_4 and CHN groups with respect to their own principal axes.

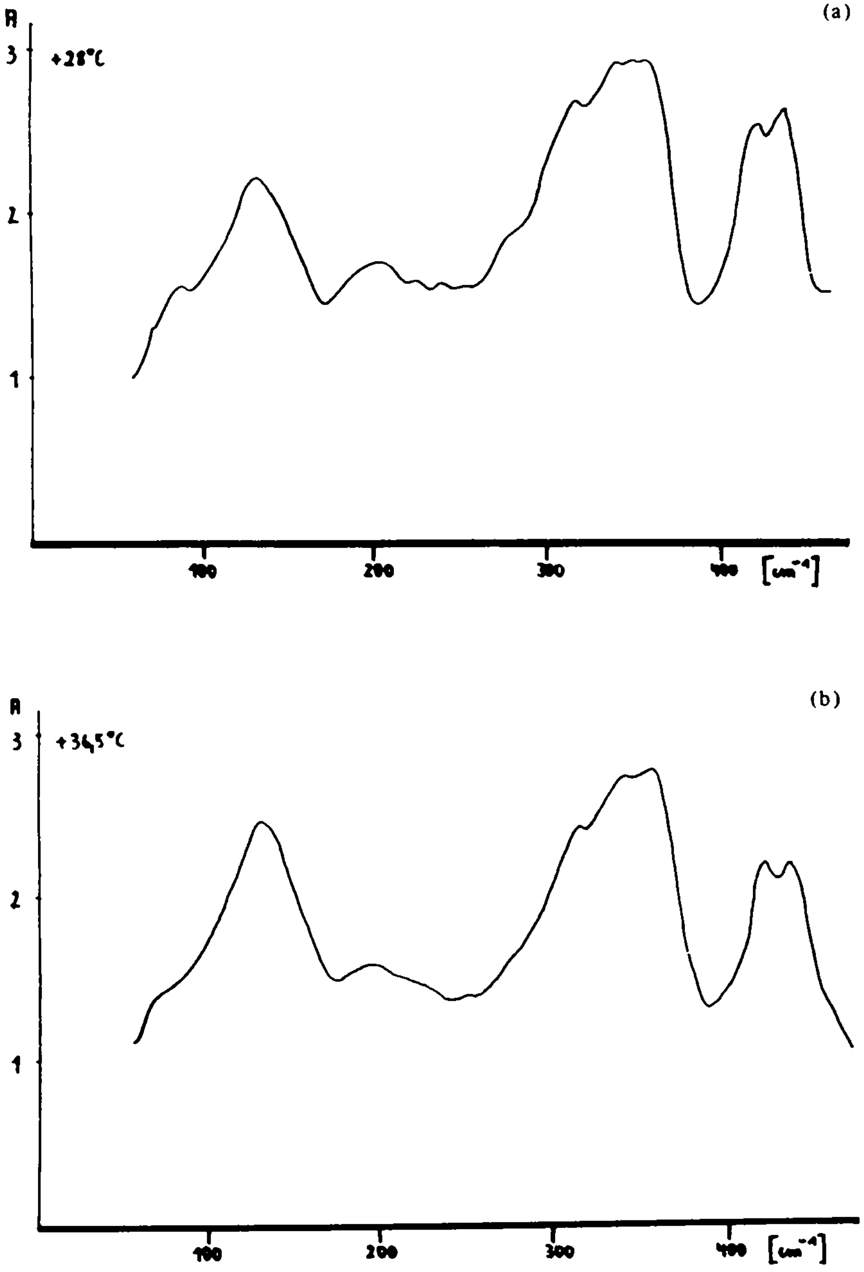


FIGURE 4 Absorption spectrum of nematic phase of MBBA at a. 28°C and b. 36,5°C.

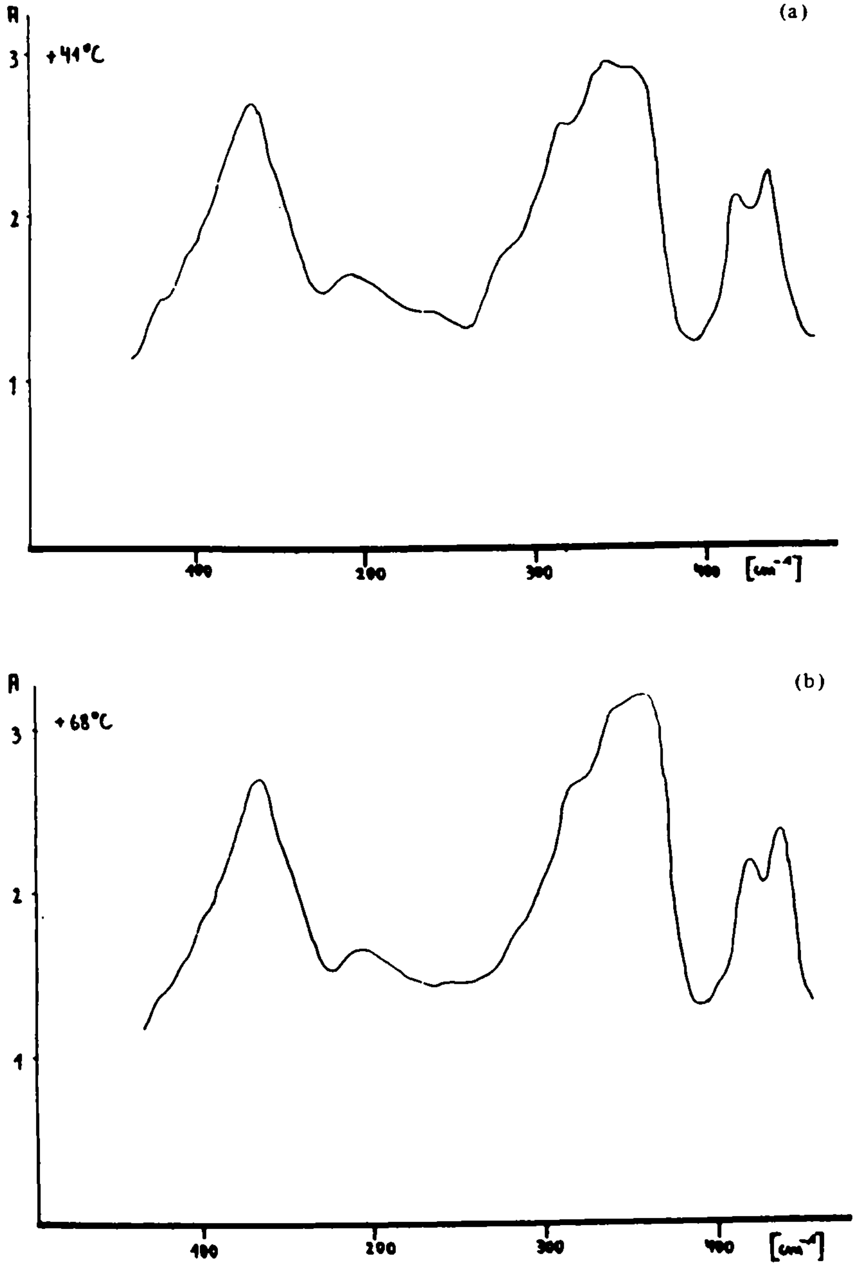


FIGURE 5 Absorption spectrum of the izotropic phase of MBBA at a. 41°C and b. 68°C.

Use of the high barrier approximation for solving the Mathieu equation yields an estimate of the energy involved in the transition between the appropriate libration levels with an assumed barrier height V for rotation (libration)

$$E = n\sqrt{\frac{V}{21}} \tag{1}$$

where: n- is the barrier multiplicity factor.

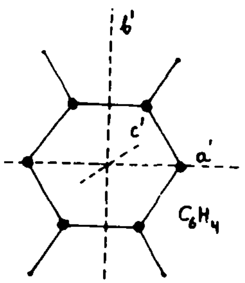
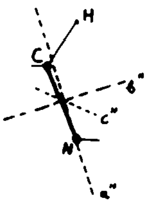
TABLE II

Calculated moments of inertia of MBBA molecule with respect to its principal axes for the assumed models, in 10^{-38} g cm^2

	Model A	Model A$'$	Model B	Model B$'$
I^a	6.23	9.83	4.34	5.46
I^b	98.9	91.5	102.1	103.8
I^c	105.7	91.5	105.6	98.7

TABLE III

Moments of inertia of C_6H_4 and CHN groups calculated on the basis of the proposed MBBA models with respect to their own principal axes

C_6H_4				CHN			
$I^{a'}$	$I^{b'}$	$I^{c'}$	10^{-38}g cm^2	$I^{a''}$	$I^{a''}$	$I^{c''}$	. 10^{-40} g cm^2
1,23	1,15	2,38		0,95	18	17,5	
							

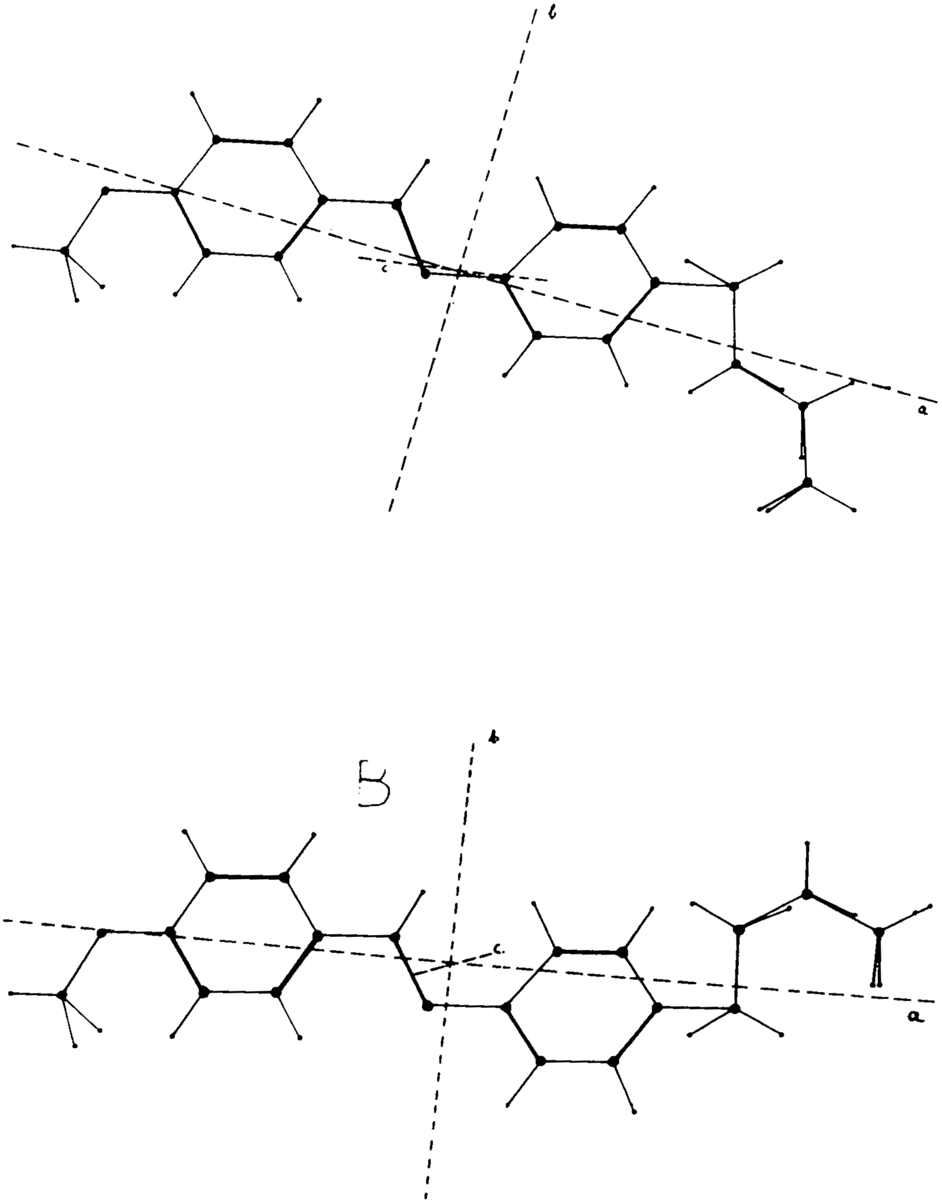
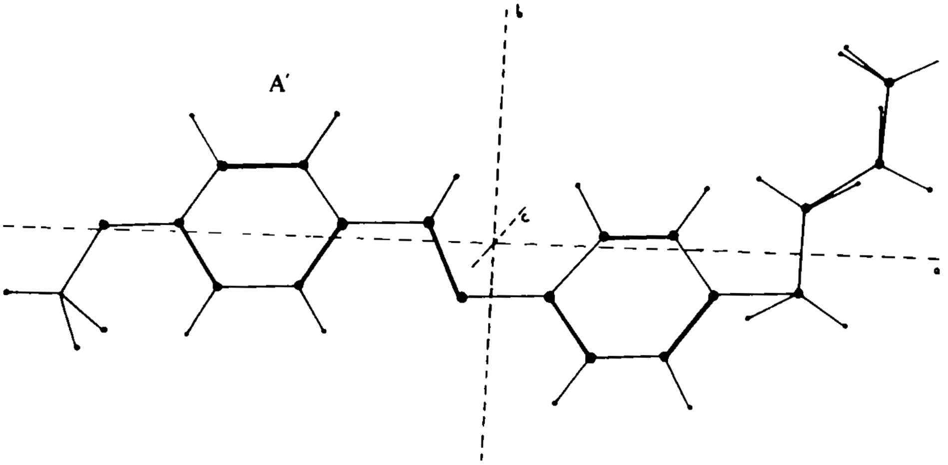
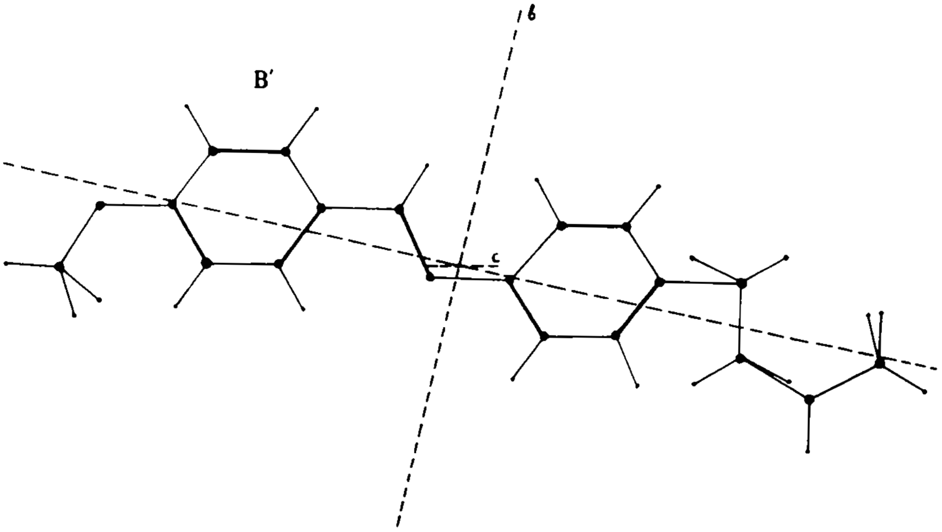


FIGURE 6 Graphical models of the MBBA molecules.

A′



B′



Assumption of the value V = 2.6 kcal/mole, obtained from dielectric measurements for the nematic phase of PAA[5], as the barrier for libration of the entire molecule with respect to the long axis and of the multiplicity factor n = 2 gives an estimated libration frequency of the molecule with respect to the long axis (a) for the various models of 13 cm^{-1} (model A), 11 cm^{-1} (model A′), 16 cm^{-1} (model B′). and 14 cm^{-1} (model B). This is certainly a rough approximation but it suggests that the frequency of ca. 100 cm^{-1} observed both in the Raman spectra[6,7] and in infra-red spectra of MBBA is probably not the frequency of libration of the whole molecule with respect to its long axis.Since, according to References[8] and[9] the vibrational mode at 100 cm^{-1} observed in aromatic compounds has its origin in the librations of the benzene rings, the relatively strong modes at 94, 102, 117, and 137 cm^{-1} in MBBA have been interpreted as libration modes of C_6H_4 rings with respect to their principal axes b and c. According to References[16,17] the same modes have been interpreted as libration modes of OCH_3 group with respect to C-OCH_3 axis. The strongest vibrations at frequencies of 340 and 360 cm^{-1} are attributed to the libration modes of the CHN group with respect to its principal traverse axes (b and c). The vibrations in the 190 to 253 cm^{-1} range are believed to be due to the OCH_3 and CCH_3 groups in the molecule,[10] whereas those in the 2.70 to 320 cm^{-1} region are presumably vibrations of the C_4H_9 group.[11]

Quite recently two papers have appeared, in which far infra-red spectra of MBBA in the region from a few to ca. 200 cm^{-1} have been reported [13, 14]. It seems that the solid MBBA spectra reported in these papers correspond either to the metastable modification or to a mixture of both: metastable and stable one. The authors of paper [14] present an interpretation of the band at ca. 130 cm^{-1} different from that suggested by us. They apply, namely, the Brot molecular dynamics model^{-1} and interpret the 130 cm^{-1} frequency as arising from the MBBA molecule libration about the long molecular axis. Such an interpretation should be considered as an alternative posibility to that suggested in this paper. However, even if it were true, one should abserve additional absorption in the 100 – 150 cm^{-1} region due to librations of benzene rings.

The existence of the pre-transition effect was observed for deuterized PAA [12]. In the 110 – 116°C soft-solid region the authors observed a change in the coherent scattering of neutrons for the crystal phase right up to the transition to the nematic phase In our case, in a temperature region of about 2°C just above the melting point (22°C) and clarification point (41°C), an apparent rise of absorption is observed for MBBA. This effect suggests the existence of a pre-transitional region in which the substance "becomes prepared" for the phase change (c-n, n-iz).

CONCLUSIONS

1) The spectra of solid MBBA in the far infra-red obtained in this study demonstrate a distinct between the two modifications of solid MBBA (stable and metastable). It is still too early to interpret this difference in the spectra, particularly as no adequate X-ray diffraction studies have yet been made which would give some notion about the structure of the two forms..

2) The observed spectra may in general be interpreted as being associated with the internal vibrational modes of MBBA molecules. The lattice vibrations of MBBA most probably appear below the frequency range investigated in this study.

3) In temperature intervals of about 2°C before the melting and clarification points a strong rise is observed in the apparent absorption of radiation in the far infra-red, presumably due to the existence of pre-transition effects. A rise in apparent absorption was also observed in the phase transition region around –50°C for the metastable form of solid MBBA.

Acknowledgements

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