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Properties of the Blue Phase in Liquid Crystalline MMBC

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The structures of the blue phases were investigated by the examination of Bragg reflections in MMBC (2-methylbutyl p[N-(p-methoxybenzylidene)-amino] cinnamate). Six selective reflection lines, to which do not apply the selection rules proposed by Hornreich and Shtrikman, were detected. The distances between lattice planes measured directly appeared to coincide well with those obtained from Bragg reflection data.

Although the blue phase was discovered nearly a century ago,[1] its structure is not yet fully apprehended. Two models of the blue phase, cubic[2–4] and one-dimensional helicoidal[5] have been proposed. Recently, the blue phase is usually recognized as a three-dimensional cubic lattice, similar to that of solid crystals. The most convincing argument for such a three-dimensional lattice is the appearance of many Bragg scattering lines, to which the appropriate Miller indices can be assigned like in the case of X-ray reflection from lattice planes of solid crystals. The blue phase has a period of a few hundreds of nm and therefore the reflections from lattice planes can be observed within the visible range of the spectrum. The optical studies of Bragg reflections are a rich source of information on the very structure of the blue phase.[6–8] Some attempts to determine the symmetry of the blue phase lattice by means of the Hornreich-Shtrikman theory[3,9] and the selection rules derived from this theory,[10] were also accomplished. Comparison of the reported results shows that it is difficult to single out one universal structure related to the blue phase, since its various modifications (BP I, BP IIa and BP IIb according to Flack and Crooker[11] notation) can have different structures. The affiliations of various forms of the blue phase to a particular space group (I23 (T^3), $I2_13$ (T^5) and $I4_132$ (O^8) space groups are frequently mentioned) were

based on the observation of a few Bragg reflections only (four lines in the best case).[7] The number of observed lines was usually insufficient e.g. for distinguishing T^3 and T^5 space groups from O^8 on the basis of the H-S selection rules one should observe at least 14 lines what is impossible because of the absorption. P23 (T^1), $P4_232$ (O^2) and I432 (O^5) space groups were assigned to various forms of the blue phase on the basis of the observation of one or two Bragg reflection lines.[8] Since so small number of observed lines cannot be used for a unique determination of crystalline symmetry Nicastro and Keyes[8] took into account that the reflection spectra do not contain certain lines. However, one should be careful with the conclusions drawn from the absence of certain lines, because not all lattice planes of the blue phase have to be oriented parallel to the sample surface, similarly like not all lattice planes of solid crystals have to be the planes of growth or splitting. Thus, the observation of a possibly highest number of lines seems to be necessary to test the H-S theory and its implications expressed in terms of selection rules.

EXPERIMENTAL

The liquid crystalline 2-methylbutyl p[N-(p-methoxybenzylidene)-amino] cinnamate (MMBC) with the clearing temperature of about 99°C, synthesized by Kodak, was used in all measurements. This material has the blue phases (BP I, BP II and the "fog phase") in the temperature range of about 0.2°C. In cholesteric phase it has an exceptionally large pitch of helix (above 0.4 μm at Ch → BP transition). Since there is a direct correlation between structure period of BP and pitch of helix in cholesteric phase, one may expect that a period of a blue phase in this material is also unusually large and the detection of many Bragg reflection lines can be realized within the visible and infra-red region only. Bragg reflections were examined with the polarizing microscope with monochromatic light. The reflections were detected visually. The visual detection is simple and seems to be better than the method of Crooker, Johnson and Flack,[7] since it allows one to register reflections from relatively small, homogeneously oriented areas of the blue phase. Apart from it we made the measurements with the IR transmitting spectrophotometer (0.7 – 2.7 μm) and the UV-Vis spectrophotometer (0.3 – 0.8 μm). The temperature of sample was stabilized with the electronic programmer Unipan 650 with the accuracy better than 0.005K.

The results are shown in Figure 1. As can be seen, six lines were

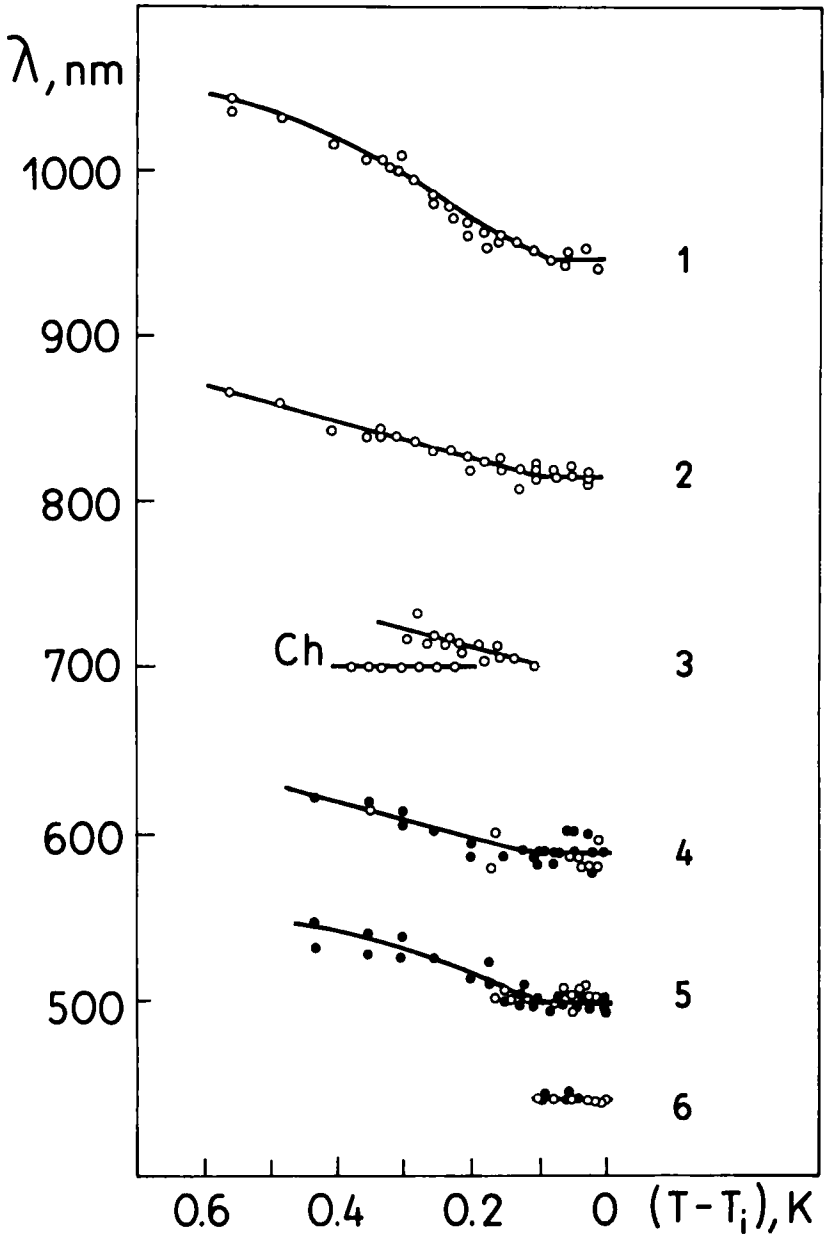

FIGURE 1 Selective reflection in the blue phases of MMBC as a function of temperature T. T_i – temperature of the transition from BP II to isotropic phase ○ – transmission, ● – back reflection.

detected; not all of them appeared in both blue phases BP I and BP II. No selective reflection from "fog phase" was noticed. All lines detected in the visible region are right circularly polarized. To supplement the selective reflection measurements we also determined the period of the BP structure with the Cano method.[12] In this case, the sample was placed between glass plate and spherical lens with the curvature radius of about 100 mm. After a very slow cooling from isotropic phase (cooling rate of about 0.01 K/min) the sample contains large areas of the same orientation with clearly visible disclinations (Figure 2). Although the mechanism of formation of these disclinations is still unknown[13] one can assume that they divide the areas in which the number of "lattice planes" per thickness of sample differs by one.

In BP II disclination lines are regularly distributed and their distances correspond to a constant increase of a thickness of sample (Figure 2). In BP I the line structure is more complicated; an increase of sample thickness from line to line is alternately larger and smaller. The complex structure of disclination lines in BP I seems to be a common feature; we observed it in numerous mixtures and pure cholesteryl esters. This feature can be used as a criterion of distinguishing BP I from BP II when only one of them appears in the material. In BP I → BP II transition the disclination lines become more regular, but their number is constant which indicates that a period of structure remains continuous in this transition. The interplanar distances determined with the above method are: (152 ± 5)nm in the direction along which the green light is selectively reflected (the orientation reflecting also the light of the longest wavelength ~1 μm) and (177 ± 2)nm in the direction along which the yellow light is selectively reflected. The pitch of helix p measured in the same way in cholesteric phase is (427 ± 5)nm at Chol → BP transition. Comparison of a pitch and a wavelength of selective reflection for cholesteric phase enables one to determine the mean value of refractive index.

$$n_{chol} = \lambda_{R_{chol}} \Big/ p_{chol} = 1.64 \pm 0.02.$$

DISCUSSION

If one assumes that the structures of both blue phases are cubic then

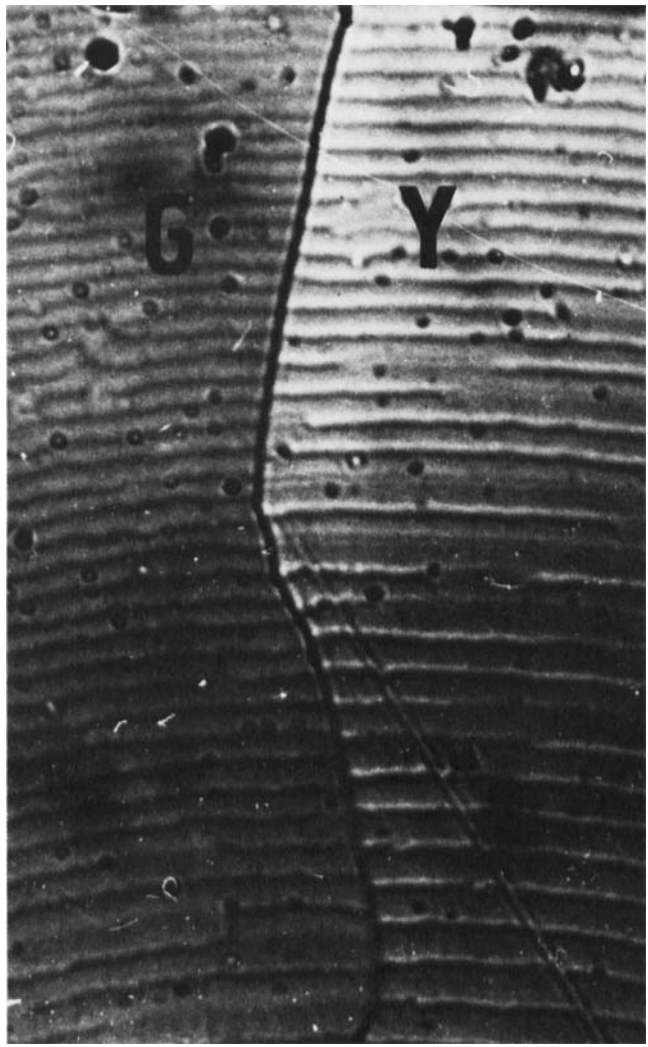

FIGURE 2 Cano-disclinations in BP II of MMBC G – green areas, Y – yellow areas.

the wavelength of selective reflection λ_R must fulfill the Bragg condition

$$\lambda_R = \frac{2\,n\,d\cos\alpha}{\sqrt{h^2 + k^2 + l^2}} \tag{1}$$

where n denotes the mean value of refractive index, d – lattice constant, α – angle of incidence, and h, k, l – Miller indices. For $\alpha = 0$ (back reflection) one obtains

$$\frac{1}{\lambda_R^2} = \frac{s}{4n^2 d^2} \tag{2}$$

where $s = h^2 + k^2 + l^2$. Relation (2) may be used for estimation of Miller indices. The dependence of $1/\lambda_R^2$ on successive integers i, should be linear as requested by relation (2). The best fitting of eq.(2) to our experimental data is shown in Figure 3. The values of λ_R in Figure 3 correspond to BP I → BP II transition.

In this way appropriate Miller indices can be assigned to the successive selective reflection lines. However, this is not a unique procedure since one may also obtain a linear dependence for $s = m \cdot i$, where m = 1,2,3 ... . Various values of m correspond to different types of cubic lattices. Some limitation concerning the Miller indices h,k,l result from symmetry.[14] For a simple cubic lattice (sc) all values of h,k,l are admissible, for a body-centered cubic lattice (bcc) the sum h + k + l have to be an even number, whereas for a face-centered cubic lattice (fcc) all indices have to be either odd or even numbers. The above rules show that for a simple lattice (sc) m = 1, for a body-centered lattice (bcc) m = 2, and for a face-centered lattice (fcc) m = 4.

Now, we can go back to equation (2) and determine a lattice constant d for various types of cubic lattice, substituting $m \cdot i$ instead of s and assuming that $n = n_{chol}$. The value of d constant enables one to calculate the interplanar distances a, $a = d/\sqrt{s}$. The results of these calculations carried out for the temperature of BP I → BP II transition are listed in Table I. The table also contains the values of interplanar distances *a* measured with the Cano method for both orientations of the blue phase. As may be noticed the values of interplanar distances obtained with the Cano method coincide very well with those determined from spectrophotometric measurements. However, the determination of m with the Cano method is impos-

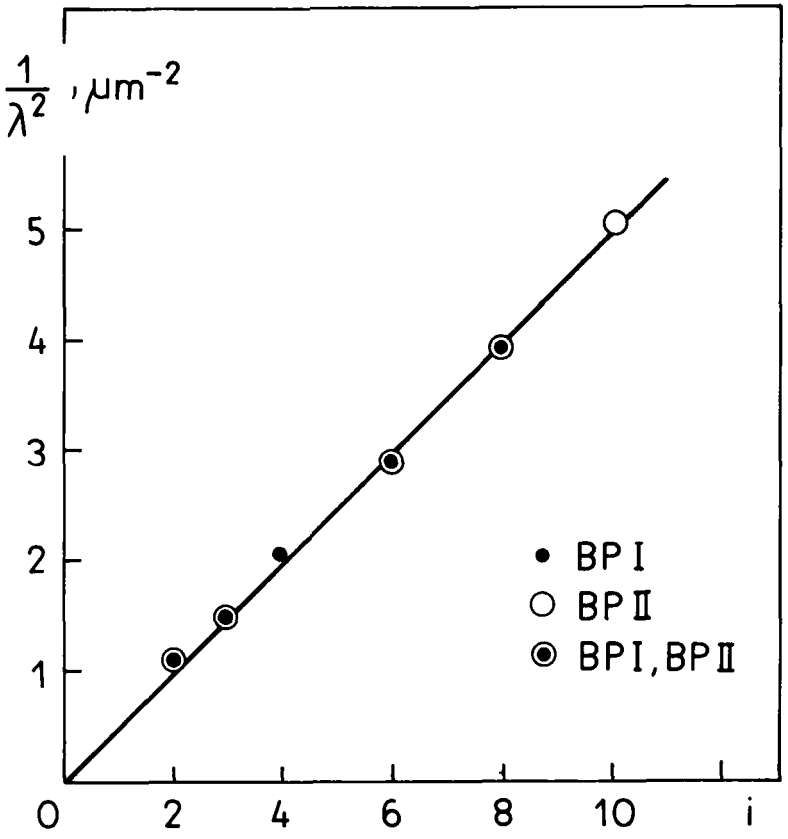

FIGURE 3 $\frac{1}{\lambda_R^2}$ as a function of succesive integer numbers.

TABLE I

Miller indices for various types of cubic lattices and interplanar distances measured with different methods.

	sc m = 1 d = 433 nm			bcc m = 2 d = 613 nm			fcc m = 4 d = 867 nm			a/nm	
	s			s		hkl	s				
R/nm	BPI	BPII	hkl	BPI	BPII		BPI	BPII	hkl	from R	from Cano method
946	2	2	110	4	4	200	8	8	220	306	
813	3	3	111	6	6	211	12	12	222	250	
710	4		200	8		220	16		400	217	
590	6	6	211	12	12	222	24	24	422	177	177
504	8	8	220	16	16	400	32	32	440	153	152
443		10	310		20	420		40	620	137	

sible, since one obtains the same interplanar distances for particular lines of selective reflection for all types of cubic lattices. An attempt to determine the lattice symmetry on the basis of the Hornreich-Shtrikman (H-S) selection rules[10] also failed. The theory of Hornreich-Shtrikman do not predict such a sequence of s as that in Table I. Since the values of λ_R are burdened with some experimental errors we cannot exclude possibilities of other assignments of $1/\lambda_R^2$ to s than that shown in Table I[15] which would fulfill the H-S rules. Attempts of such an indexing can start from $s=4$, since reflection from (111) planes ($s=3$) is forbidden by the H-S rules in all cubic lattices, and fitting the experimental data to smaller values of s (excluding $s=3$) fails. Then, the following sequences of s agree fairly well with the experiment:

$s = 4, 5 \text{ or } 6, 8, 10 \text{ or } 11, 14 \text{ or } 16$ for BP I

$s = 4, 5 \text{ or } 6, 10 \text{ or } 11, 14 \text{ or } 16, 18 \text{ or } 19$ for BP II.

Since the second line ($s=5$ or 6) does not fulfil the crystallographic selection rules for fcc lattice, only sc and bcc lattices remain to be considered.

Should the looked for lattice be simple one would observe within the investigated range of spectrum (0.4 – 2.7 μm) at least 13 lines of selective reflection, whereas for a bcc lattice the number of lines would be reduced to seven. In experiment we observed only five lines. Thus, it is difficult to believe that so many lines were missing due to an unsuitable orientation of the blue phase platelets. On the contrary, the reflection from (100) planes should be registered since the lattice (200) planes (to which the (100) planes are parallel) give a reflection (line 1 in Figure 1). Similar situation occurs for (110) planes, which should reflect according to the H-S rules in all sc and bcc lattices, but no appropriate line is observed in experiment. However, the line from (220) plane ($s=8$) which is parallel to (110) is observed. A similar problem occurs with 3 and 6 lines which are visible in one of the blue phases but vanish in the other.

Thus, the above possibility of indexing must be also rejected. Altogether, it leads to the conclusion that the H-S selection rules do not apply to the investigated material. Therefore, the H-S rules cannot be used as a criterion for indexing, and neither of the logical possibilities presented in Table I can be excluded.

It is also worth noticing that for the bcc lattice the (220) line has the same wavelength as the reflection line in cholesteric phase, it

means that the cholesteric pitch equals to the interplaner distance for the (220) planes. Thus, if the blue phases in MMBC are bcc then their molecular ordering should be different from that proposed in the reported up to now models.[3,4]

Some doubts may result from the fact that we did not detect the reflections in IR region, but the transmissions only. Neither we were able to check a polarization of IR-lines. However, the analogy to other materials with the blue phases shows that these lines should be also found in reflection spectrum. For example, line 1 (Figure 1) appears at wavelength of about $\sqrt{2}$ greater than selective reflection in cholesteric phase, similarly like in the blue phases of other materials. Flack and Crooker[11] showed that a line of the highest wavelength appears in the back reflection and has a circular polarization, which agrees with our observations for other materials.

The wavelength of the successive line 2 (Figure 1) is 1.16 times smaller than this of line 1. We observed lines with such a wavelength ratio also in mixtures of ZLJ 1612 (Merck's nematic) and CB 15 (BDH). Since in these mixtures the line is placed in the visible region of spectrum we found that it was reflected back and that its polarization was circular. Similar observations were reported by Nicastro and Keyes[8] for some cholesteryl esters. That is why, we can easily assume that the 813 nm line in the blue phase of MMBC is also the reflection line with circular polarization.

Eventually, let us notice that no jump of wavelength of the selective reflection was observed at the BP I → BP II transition. This is the first observation of such a behaviour in the pure material. Therefore, BP II in MMBC should be classified as BP IIb according to Flack and Crooker notation.[11]

CONCLUSIONS

Our observations showed that BP I and BP II in MMBC have different structures. This conclusion results from the fact that some Bragg lines do not appear in both phases. The same may be concluded from the observation that the Cano lines in BP I are asymmetric, whereas in BP II are symmetric. The observed selective reflection lines do not fulfill the Hornreich-Shtrikman selection rules. Probably the theory of Hornreich-Shtrikman do not apply to the investigated material.

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