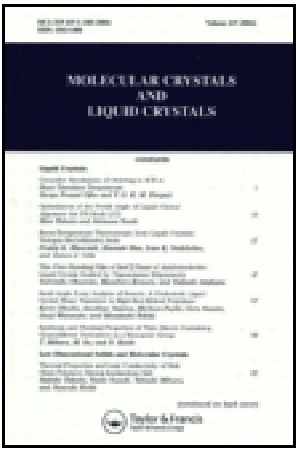

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Structure of Films Formed from Lyotropic Liquid Crystal Phases of Dyes. 1. Benzopurpurin - 4B

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STRUCTURE OF FILMS FORMED FROM LYOTROPIC LIQUID CRYSTAL PHASES OF DYES.
1. BENZOPURPURIN - 4B.

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Abstract. The films aligned by drawing thin lyotropic liquid crystal layers of benzopurpurin-4B were investigated by X-ray and electron diffraction methods. The analysis of diffraction data was carried out by straighforward (Patterson synthesis) and model procedures. The film structure is crystalline on the microlevel. Molecules are packed in monoclinic lattice (a=27A, b=7.2Å, c=59.5Å, β=141°) corresponding to space group C2/c. This model explains the type geometry of molecular aggregates in the lyotropic liquid crystal phase of benzopurpurin-4B.

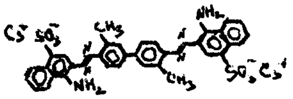
Keywords: polarizing films, dye, structure, electron diffraction, lyotropic liquid crystal, benzopurpurin-4B

INTRODUCTION

The extraordinary behavior of benzopurpurin-4B (BP) water solutions is known since the twenties. Much physical-chemical research in solutions of BP and some dyes with similar chemical structures (1-3) was performed to explain this peculiarity. Critical concentrations of micelle formation (CCM) and average number of molecules in micelles of BP and dyes of similar chemical structure were established in (4). CCM are approximately equal for these dyes but the number of molecules in micelles of BP is larger. The extraordinary behavior of BP seems to be due to the structure peculiarity of the unit micelle of BP. The purpose of this paper is to determine the structure of BP micelles. Optical investigations of the films aligned from lyotropic liquid crystal phase of BP have showed that there were not disordering processes after water substance evaporation. It is clear that film structure investigations are important to understand the process of molecular aggregation resulting in liquid crystal phase formation in water systems.

EXPERIMENTAL

In the present work the structure of films of benzopurpurin-4B was studied by X-ray and electron diffraction. The molecule is shown below. The films were aligned by drawing thin lyotropic liquid crystal layers on glass substrata.



In electron diffraction measurements the films were transferred from the plane substrata to a copper grid. Electron diffraction patterns were obtained with electron microscope EM 100L at voltage of 75 kV.

In the case of X-ray experiments the films of dye were formed many times on a glass tube of 6 mm diameter. X-ray patterns were obtained with Ni-filtered CuK$_\alpha$ radiation in UKR-3 camera on flat photographic film.

Electron and X-ray patterns were determined with a Perkin Elmer microdensitometer PDS 1010A.

Bragg spaces from electron patterns were determined by TlCl calibration (small spacing) or were calculated considering $\lambda = 0.0418\,\mathring{A}$ and a sample-photographic plate distance of 803 mm by means of Bragg equation (long spacing).

Short range order in molecular packing and molecular conformation were determined from X-ray patterns. For this purpose the Patterson function was calculated in the form

$$Q(r,z) = 2\cdot\int_0^\infty\int_0^\infty I(R,Z)\cdot J_0(2\pi rR)\cdot\cos(2\pi zZ)\cdot 2\cdot\pi\cdot R\cdot dR\cdot dZ$$

where I(R,Z) in the X-ray intensity, $J_0(2\pi rR)$ the zero order Bessel function, r and Z are direct coordinates, R and

Z are reciprocal coordinates. The molecular convolution $\overset{2}{\tilde{\rho}}$ (r,z) was constructed by means of vector method and was adapted to zero zone of Q(r,z) by varying molecular conformation. The adapted $\overset{2}{\tilde{\rho}}$ (r,z) gave the possibility to reveal the system of multiple maxima on Q(r,z) and to determine a model for the nearest molecular environment.

The order parameter was calculated from the azimuthal expansion of meridian reflections on electron patterns

$$S = 1 - (3/2)\cdot\left(\int_0^{\pi/2} \sin^3\alpha\cdot I(\alpha)\cdot d\alpha\right)/\left(\int_0^{\pi/2} \sin\alpha\cdot I(\alpha)\cdot d\alpha\right)$$

where S is the orientation degree, α the azimuthal angle, I(α) azimuthal distribution of intensity in the diffraction maximum.

RESULTS AND DISCUSSION

Electron diffraction patterns of benzopurpurin-4B correspond to crystal sample with the texture, showed in fig.1. The estimate of disorientation angle of the aggregate units gave the value in 10 degrees of circle. In this case the orientation degree is equal to 0.96.

For interpretation of electron patterns the following conditions were taken into consideration:

1) one of the translations of crystal lattice of benzopurin-4B must be long, because spacing longer than 40 Å, is observed along the layer lines;

2) this translation must be formed by longitudinal size of molecules;

3) long axes of molecules are perpendicular to the axis of texture;

4) the space group must contain the symmetrical elements, resulting in the extinguishing of meridian reflections on the odd layer lines;

5) we must take into consideration that forbidden reflections may take place on electron patterns;
6) the molecular packing in unit cell must be filling;
7) when modeling the packing it is necessary to consider the possibility of the existence of intermolecular hydrogenous bonds.

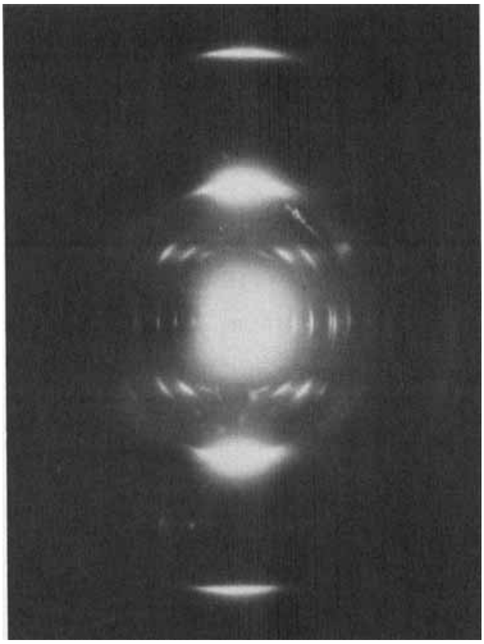


FIGURE 1. Electron diffraction pattern of benzopurpurin - 4B.

The geometry of the electron pattern of BP corresponds to a rectangular section of monoclinic or orthorombic lattice. The latter can be discarded, because the filling of molecular packing is not complete. Here M,E and C are meridian, equatorial and layer reflection respectively.

In the monoclinic system there are several variants of lattices that more or less correspond to diffraction data. The lattices with parameters: a=27.0 Å, b=7.2 Å, c=53.5 Å and β =141° are preferred. The "b" translation is consistent with the direction of the texture axis. There are two variants of space groups for the packing of plane molecules: $P2_1/c$ (the extinguishing law: L for HOL and K for OKO) and

TABLE 1. Electron diffraction and structure data

Reflection	Bragg periods		
	experimental (Å)	calculated (Å)	HKL
E	16.65 ± 0.50	16.85	002
E	11.4 ± 0.1	11.23	003
E	8.47 ± 0.1	8.42	004
E	6.54 ± 0.08	6.74	005
E	4.90 ± 0.07	4.81	007
E	4.31 ± 0.07	4.21	008
E	3.80 ± 0.07	3.74	009
E	3.41 ± 0.06	3.37	0010
E	3.11 ± 0.06	3.07	0011
E	2.90 ± 0.06	2.80	0012
E	2.68 ± 0.05	2.69	0013
E	2.17 ± 0.05	2.15	0014
M	3.38 ± 0.05	3.60 3.40	020 500
M	2.44 ± 0.05	2.40	030
M	1.67 ± 0.05	1.80	040
C	6.34 ± 0.08	6.65 6.35 6.23	113 213 212
C	5.38 ± 0.07	5.54 5.11	216 203
C	4.76 ± 0.07	4.58 4.55	212 114

C2/c (the extinguishing law: H+K for HKL, H, L for HOL and K for OKO) (6). Both variants seem to be equivalent, because there is uncertainty on the determination of the extinguishing law H+K for reflections HKL. This fact is shown by two dimensional diffraction effects and errors of measuring of diffraction angles.

Calculated meridian periods (on the base of chosen lattice) are a little bit longer than experimental periods determined from electron diffraction pattern, but they well coincide with the data of X-ray experiment and with the thickness of benzene circle.

X-ray patterns of BP (fig.2-a) can be easily indexed in terms of the previously discussed lattice, tab.2.

TABLE 2 X-ray diffraction and structure data.

	Bragg periods		
HKL	experimental (Å)	calculated (Å)	
002 100	16.80±0.25	16.85	17.0
003	11.24±0.08	11.23	
004 200	8.56±0.05	8.42	
005	6.70±0.05	6.74	
007	4.85±0.05	4.81	
008 400	4.27±0.05	4.21	4.25
500	3.45±0.04	3.40	
020	3.62±0.04	3.60	
112	5.66±0.05	5.61	

The lattice parameters are more precisely determined from X-ray data, because the definition of periods is more precise.

The analysis of Patterson function (ZY section) with regard to molecular convolution demonstrates that flat molecular conformation is more preferable, fig.2-b,c.

The chains of strong maxima, aligned along Z, are situated 3.6 Å apart from each other (the size of molecular packing period along "b" lattice translation). We may note that maxima in even chains (zero and second) coincide, but maxima in the first chain are moved along Z by 14 Å. This means that neighbour (on "b" translation) molecules translate relatively to each other by half of their length. This structure motive corresponds to space group C2/c. Molecular packing for this case is shown in fig.3.

CONCLUSIONS

As a result of diffraction study of films of benzopurpurin-4B it stands to reason that molecules of BP have plane trans-conformation and they are packed in monoclinic lattice (space group C2/2). In this molecular packing there is strong cohesion between molecules lying in plane of "b" and "c" translations (plane molecular contacts

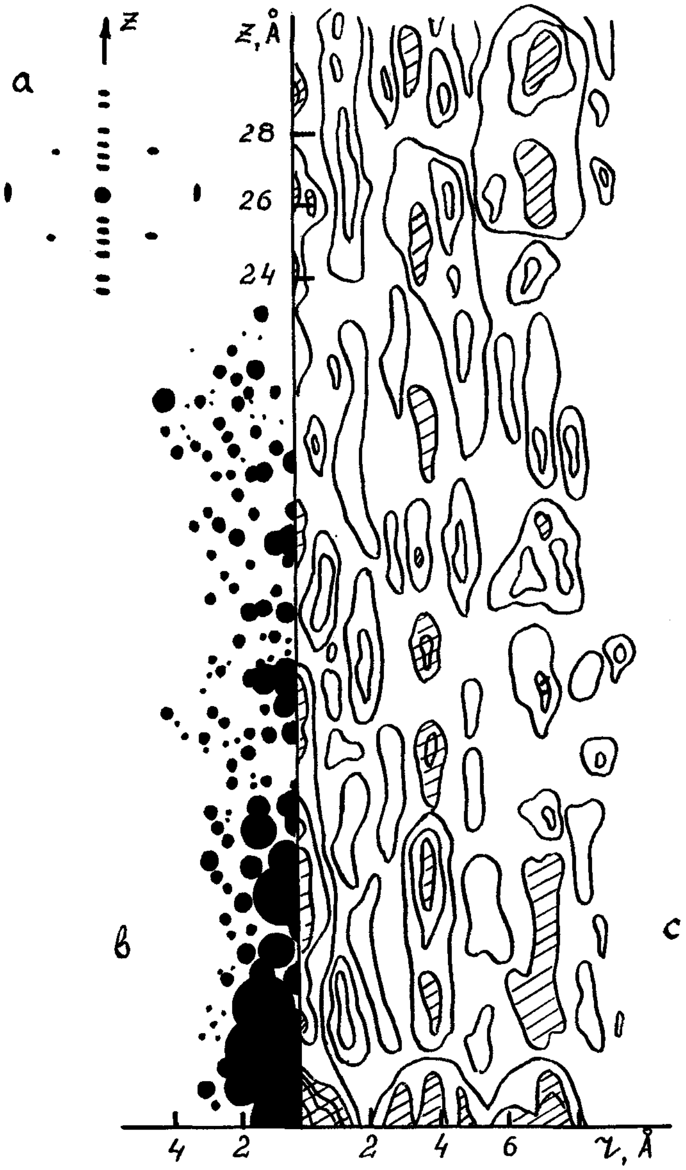


FIGURE 2. Structure data for BP : X-ray pattern (a); molecular convolution (b); Patterson map (c).

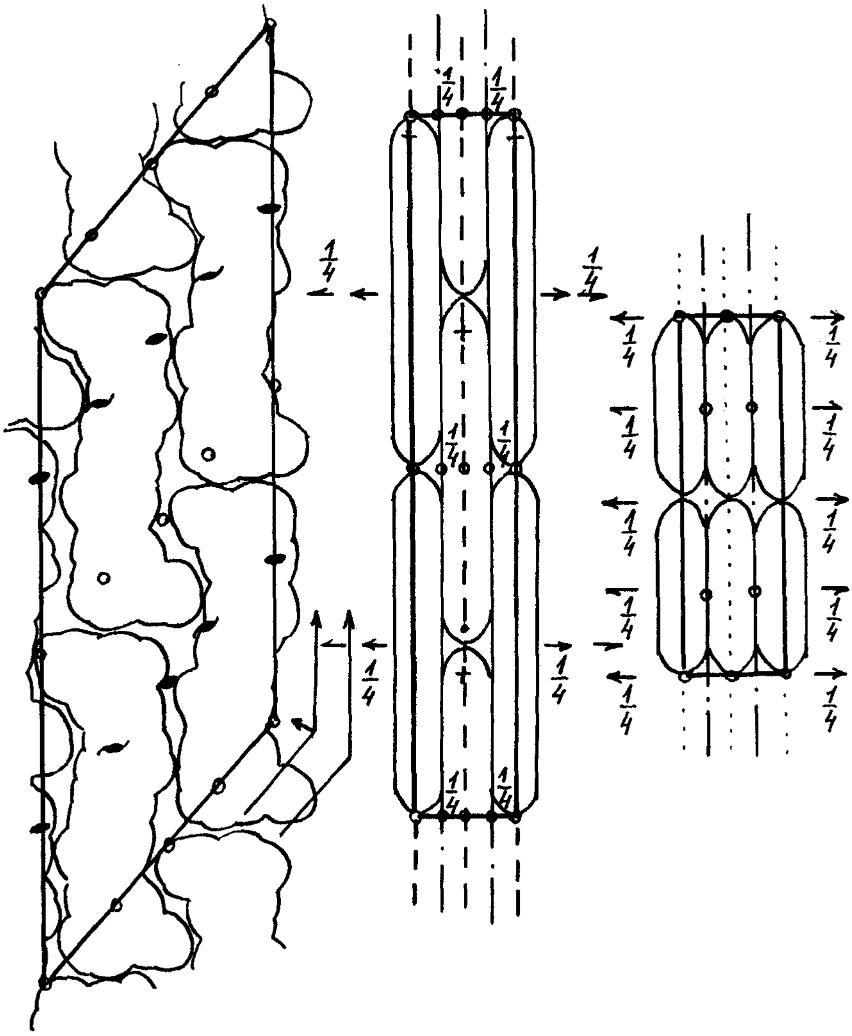


FIGURE 3. Molecular packing of benzopurpurin-4B.

with overlap), and relatively weak cohesion between next molecular "bc"-planes (edge molecular contacts). Thus it appears that building units of crystal lattice are quasi-two dimensional aggregates. So called "breakwork" structure motive in molecular packing of film are inherited from the primary lyotropic liquid crystal phase of BP, thus we may suppose that molecular aggregates in LLC phase must have the tape geometry.

REFERENCES

1. C.Robinson, H.A.T.Mills, Pros. Roy Soc. (London, 1931), A 131, p. 576-611.
2. C. Robinson, J.L.Moillet, Pros. Roy Soc. (London, 1934), A 147, p. 630-654.
3. H.P.Frank, J.Colloid Sci., (1957), 12, p. 480-495.
4. R.S.Sivaraga Iyer, J.S.Singh, Colloid Z und Z. Polymere, (1970), 242, p. 1196-1200.
5. B.K.Vainstain, X-ray diffraction on chain molecules, (Academy Sci. of the USSR, Moscow, 1963), p. 372.
6. G.B.Bokii and M.A.Porai-Koshits, Practical-Course of X-ray, (Moscow University, Moscow, 1951), p. 430.