

# J-aggregate-like Structure and Its Influence on the Electronic Spectrum of 1,4-diketo-3,6-bis(4-biphenyl)pyrrolo[3,4-c]pyrrole

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The title compound (BP-DPP), known as a red pigment as well as a photoconductor for photoreceptors, is characterized by an extremely large bathochromic shift upon crystallization, as compared with other DPP analogues. The electronic structure of BP-DPP has therefore been investigated from the standpoint of crystal structure and exciton coupling effects. BP-DPP is found to crystallize in the “bricks in a brick wall” fashion, just like J-aggregates in cyanine dyestuffs. On the molecular plane of BP-DPP, there are chains of intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one. The hydrogen bond aligns the transition dipoles in a fashion “head-to-tail”, leading to a bathochromic displacement of the absorption maximum. Additionally, there are diagonal pairs of the brick wall structure whose exciton coupling again induces a bathochromic shift. Both the hydrogen bond in the molecular plane and the brick wall structure along the molecular stack are found to displace significantly the absorption band toward longer wavelengths on going from solution to the solid state.

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## Introduction

Diketopyrrolopyrrole (abbreviated to DPP) pigments are industrially important red pigments based on the novel diketopyrrolopyrrole chromophore.<sup>1</sup> DPPs are used as imaging colorants as well as in color filter arrays for liquid crystal display applications. On the other hand, dithioketopyrrolopyrrole (DTPP) has attracted attention as a material for photoconductors for laser printers<sup>2</sup> and for optical disks<sup>3</sup> operating at 780 nm, based on GaAlAs laser diodes.

Up until now, five DPP-derivatives have been on the market (Fig. 1), and most of their structures have already been analyzed: *p*-Cl DPP,<sup>4</sup> DPP,<sup>5</sup> TB-DPP,<sup>6</sup> and *m*-CN DPP.<sup>7</sup> Although the absorption spectra of these derivatives are not so different in solution, the colors in the solid state change variously, depending on the molecular arrangement. For example, *p*-Cl DPP bears a vivid red color (absorption maximum: 540 nm) while the absorption maximum is displaced toward shorter wavelengths in the order of DPP, TB-DPP and *m*-Cl DPP in accordance with the increase in yellowness. The correlation between the crystal and electronic structures of DPP pigments, except for BP-DPP, has already been discussed in our previous article from the standpoint of crystal structure and exciton coupling effects.<sup>8</sup> The results are fully consistent with experiment.<sup>9,10</sup>

On the other hand, the title compound (1,4-diketo-3,6-bis(4-biphenyl)pyrrolo[3,4-c]pyrrole; BP-DPP) exhibits a shade of bluish red and has the longest wavelength

absorption band (*ca* 560 nm) among DPP pigments. This remarkable bathochromic effect is one of the long-standing problems in DPP pigments. In the course of our investigation on the electronic structure of dithioketopyrrolopyrrole (DTPP), we have encountered a similar effect of an extremely large bathochromic shift, into the near-IR region,<sup>11,12</sup> only when the molecules are arranged in the “bricks in a brick wall” fashion, just like J-aggregates in cyanine dyestuffs.<sup>13</sup> Interesting to say, the molecular symmetry changes from  $C_i$  to  $C_2$  in DTPP on going from solution to the solid state, accompanied by an appearance of a small dipole moment of about 0.27 *D*. As a consequence of the dipole moment, the molecules can arrange themselves pairwise in the “bricks in a brick wall” fashion so as to reduce the electrostatic energy. This consideration suggests that the appearance of a dipole moment upon crystallization is prerequisite for the formation of the brick wall structure. The molecular symmetry of BP-DPP ( $C_i$ ) is, at first sight, likely to be lowered upon crystallization to give rise to a dipole moment, because the angles at the single bonds (between the phenyl rings and/or between the phenyl and heterocyclic rings) on each side of the heterocyclic ring system can be twisted asymmetrically. This leads to reduction in molecular symmetry, for example, from  $C_i$  to  $C_1$ . Based on this idea, we assumed that BP-DPP should crystallize in a brick wall structure.

The purpose of the present investigation is to determine the crystal structure of BP-DPP and characterize the electronic structure.

## Experimental Section

### Crystal Growth of Single Crystals and Preparation of Evaporated Films

BP-DPP was obtained from Ciba Specialty Chemicals. The single crystals were grown from the vapor phase in

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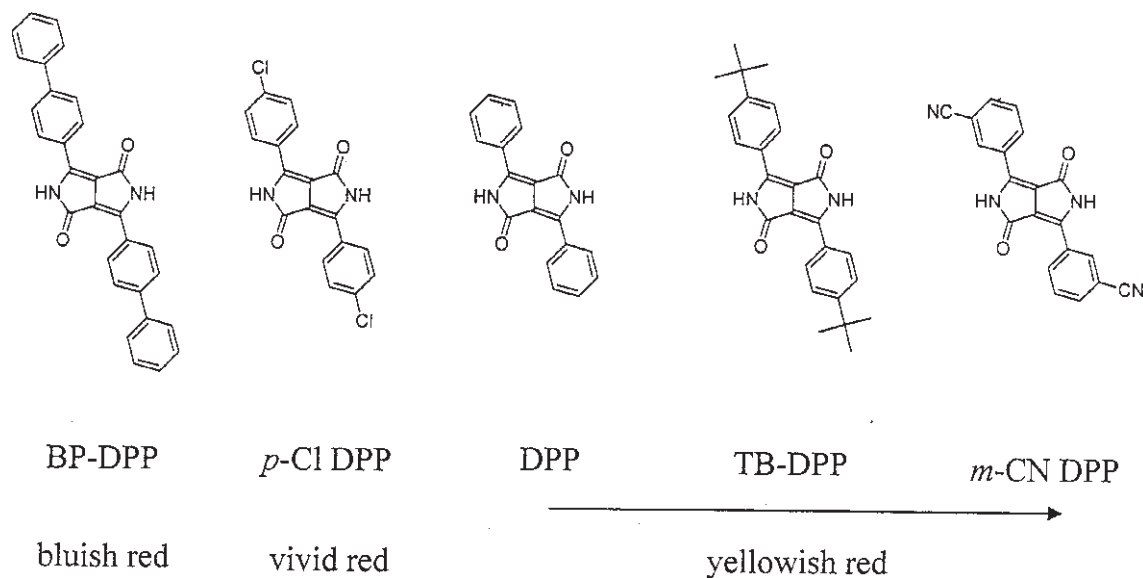


Figure 1. DPP pigments and their colors.

a closed system using a two-zone furnace.<sup>14</sup> The crystal structure was analyzed by a Rigaku X-ray diffractometer AFC7R. The evaporated films of BP-DPP were prepared under high vacuum onto glass substrates for measurements of absorption spectra (thickness: *ca* 800 Å).

#### Measurements

The solution and solid state spectra were measured on a Shimadzu spectrophotometer (UV-2400PC). The temperature dependence of the absorption spectra of evaporated BP-DPP was measured in the range between 20 and 270 K in increments of 50 K in combination with a cryostat from Iwatani Gas Co. Ltd. (model: CRT-105-OP). Polarized reflection spectra were measured on single crystals of BP-DPP by means of a UMSP 80 microscope-spectrophotometer (Carl Zeiss) equipped with an R928 photomultiplier (HTV). An Epiplan Pol (×8) objective was used together with a Nicol-type polarizer. Reflectivities were corrected relative to the reflection standard of silicon carbide.

### Results and Discussion

#### Crystal Structure

The crystal data of BP-DPP as well as the fractional coordinates for non-hydrogen atoms are given in Tables I and II, respectively. Details of the structure are given in Ref. 15. Figure 2 shows the molecular conformation of BP-DPP. The molecule is deformed, as characterized by molecular symmetry  $C_1$ . The two phenyl rings on each side of the heterocyclic ring system are twisted asymmetrically in opposite directions. In addition, the heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of 175.7(3)°. Due to this deformed structure, a dipole moment of 0.18 *D* appears perpendicular to the molecular plane as calculated by MOPAC93.<sup>16</sup>

Figures 3(a) and 3(b) show the molecular arrangement of BP-DPP and its schematic representation, respectively. It is apparent that the molecules are arranged in the “bricks in a brick wall” fashion. There are two kinds of stacking columns: one is composed of the molecules with an upward dipole moment while the neighboring

TABLE I. Crystallographic Parameters of BP-DPP

Chemical formula	$C_{30}H_{20}N_2O_2$
Molecular weight	440.50
Molecular symmetry	$C_1$
Crystal system	triclinic
Space group	$P\bar{1}$
<i>Z</i>	2
<i>a</i> (Å)	7.226(2)
<i>b</i> (Å)	21.886(4)
<i>c</i> (Å)	6.793(5)
$\alpha$ (°)	95.25(3)
$\beta$ (°)	90.18(4)
$\gamma$ (°)	93.82(2)
<i>D<sub>x</sub></i>	1.371
<i>R</i>	0.073

column comprises the molecules with a downward dipole moment. The polar molecules are stacked pairwise so as to reduce the electrostatic energy. The present molecular arrangement is in complete agreement with that of modification III of DTPP.<sup>11</sup>

On the other hand, in the molecular plane along the *a*-axis, there are chains of intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one. This forms a two-dimensional hydrogen bond network as found in all DPP pigments<sup>4–7</sup> (N1/O1 = 2.803(6) Å, N1/H = 0.88(7) Å, H/O1 = 1.92 Å and N1-H···O1 = 178(7)°; N2/O2 = 2.800(6) Å, N2/H = 0.93(7) Å, H/O2 = 1.88 Å and N2-H···O2 = 178(7)°).

#### Polarized Reflection Spectra

Figure 4 shows the polarized reflection spectra measured in the (010) plane of BP-DPP single crystals. Prominent reflection bands appear around 560 and 520 nm for polarization parallel to the *a*-axis. In addition, a small reflection shoulder is also recognized around 475 nm. On the other hand, polarization perpendicular to the *a*-axis quenches these visible bands. It is important to note that the two visible bands and the reflection shoulder appear and disappear simultaneously by

TABLE II. Fractional Coordinates of BP-DPP

Atoms	x	y	z
O(1)	1.0836(5)	-0.0653(2)	0.1742(7)
O(2)	0.4046(5)	0.0683(2)	0.3275(7)
N(1)	0.4638(7)	-0.0323(3)	0.2194(8)
N(2)	1.0245(7)	0.0348(2)	0.2910(8)
C(1)	0.9714(8)	-0.0255(3)	0.2151(9)
C(2)	0.7718(8)	-0.0273(3)	0.2104(9)
C(3)	0.6145(8)	-0.0665(3)	0.1747(9)
C(4)	0.5925(9)	-0.1318(3)	0.1046(9)
C(5)	0.4238(9)	-0.1662(3)	0.1196(10)
C(6)	0.4082(9)	-0.2285(3)	0.0502(10)
C(7)	0.5577(9)	-0.2578(3)	-0.0351(9)
C(8)	0.7272(8)	-0.2227(3)	-0.0487(10)
C(9)	0.7446(8)	-0.1605(3)	0.0219(10)
C(10)	0.5419(9)	-0.3236(3)	-0.1091(9)
C(11)	0.4255(9)	-0.3661(3)	-0.018(1)
C(12)	0.4119(10)	-0.4276(3)	-0.086(1)
C(13)	0.514(1)	-0.4487(3)	-0.248(1)
C(14)	0.628(1)	-0.4074(3)	-0.341(1)
C(15)	0.6421(9)	-0.3452(3)	-0.272(1)
C(16)	0.5181(8)	0.0289(3)	0.2817(9)
C(17)	0.7174(8)	0.0318(3)	0.2764(9)
C(18)	0.8756(8)	0.0700(3)	0.3247(9)
C(19)	0.8954(9)	0.1345(3)	0.3980(10)
C(20)	1.0644(8)	0.1609(3)	0.4793(9)
C(21)	1.0830(8)	0.2228(3)	0.5491(10)
C(22)	0.9339(9)	0.2606(3)	0.5358(9)
C(23)	0.7672(9)	0.2335(3)	0.456(1)
C(24)	0.7471(9)	0.1718(3)	0.3876(10)
C(25)	0.9547(8)	0.3267(3)	0.6118(9)
C(26)	1.0702(10)	0.3467(3)	0.772(1)
C(27)	1.089(1)	0.4089(3)	0.842(1)
C(28)	0.992(1)	0.4516(3)	0.752(1)
C(29)	0.8787(10)	0.4312(3)	0.590(1)
C(30)	0.8588(9)	0.3705(3)	0.521(1)

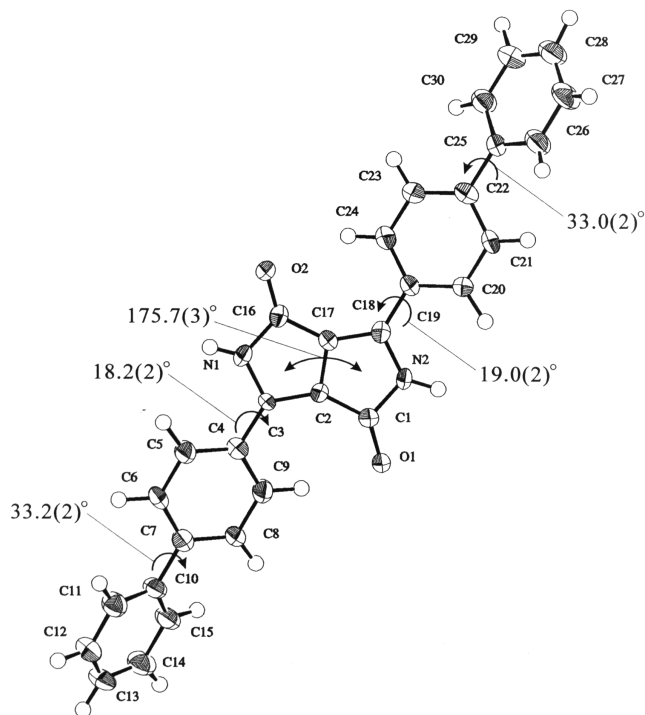
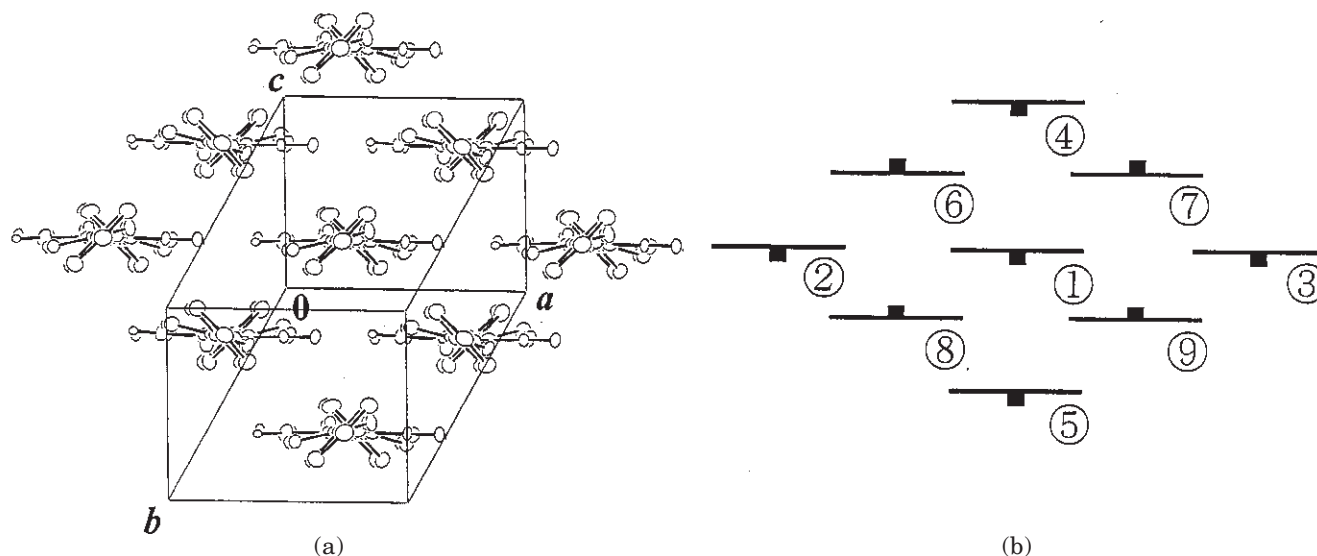
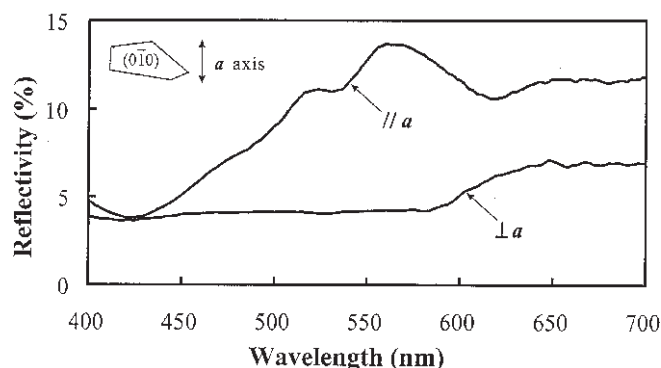


Figure 2. Molecular conformation of BP-DPP.

polarized light. This indicates that these bands belong to the same electronic transition and that the longest wavelength band is attributed to the 0-0 transition; the second-longest band (520 nm) is assigned to the 0-1, and the reflection shoulder (475 nm) to the 0-2. It is also evident that the transition dipole lies along the *a*-axis that is the direction of the intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one (Fig. 3). This also agrees with the results of other DPP derivatives<sup>6-8</sup> and DTPP.<sup>11</sup>



**Figure 3.** Molecular arrangement of BP-DPP, showing a “bricks in a brick wall” structure: (a) crystal structure and (b) schematic view. There are intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one along the *a*-axis: (N1/O1=2.803(6) Å, N1/H=0.88(7) Å, H/O1=1.92 Å and N1-H···O1=178(7)°; N2/O2=2.800(6) Å, N2/H=0.93(7) Å, H/O2=1.88 Å and N2-H···O2=178(7)°). For the numbering of atoms, see Fig. 2.



**Figure 4.** Polarized reflection spectra measured on the (0–10) plane of BP-DPP single crystals.

There is another thing to be noted in the polarized reflection spectra (Fig. 4); a gradual increase in reflectivity appears from about 600 to 650 nm, followed by constant reflectivity up to 700 nm for polarization along or perpendicular to the *a*-axis. This is due to the reflection from the rear plane of the single crystal, i.e., (010) plane. This often occurs in general in spectral regions where no absorption bands exist.

### Spectral Displacements Due to Interactions Between Transition Dipoles

Because the absorption coefficient of BP-DPP, which is proportional to the square of the transition dipole, is quite large (ca  $3.71 \times 10^4 \text{ cm}^{-1}$  in dimethylsulfoxide), it is likely that interaction between transition dipoles (“exciton coupling”) will occur in the solid state. This may lead to band splitting or spectral shifts toward longer or shorter wavelengths, depending on the geometrical arrangement of the transition dipoles. The interaction energy is given by the following dipole–dipole equation<sup>17</sup>:

$$\Delta E_{\text{exciton}} = |\mu|^2 (1 - 3\cos^2\theta) / r^3, \quad (1)$$

where  $\mu$  denotes the transition dipole,  $r$  and  $\theta$  the distance and angle between two transition dipoles. The term  $(1 - 3\cos^2\theta)$  determines the direction of the spectral shift. The bathochromic or hypsochromic shift depends on the critical angle of  $\theta = 54.7^\circ$ , below which the former will result and above which the latter will be the case.

The exciton displacement energies have been calculated for translationally-equivalent molecules as well

as translationally-inequivalent ones as shown in Fig. 3(b). The distance  $r$  and angle  $\theta$  were directly obtained from the crystal structure. The transition dipole  $\mu$  was calculated on the basis of the X-ray  $x$ ,  $y$ ,  $z$  coordinate sets using the INDO/S Hamiltonian.<sup>18</sup>

The results are given in Table III. The numbering of the molecules in Table III corresponds to that in Fig. 3(b). Of 14 nearest-neighbor molecules around molecule ①, eight major molecules [② – ③] are considered in the present calculations. The plus or minus sign denotes the hypsochromic or bathochromic shift, respectively. The molecule pairs ① ② and ① ③ are the hydrogen bond pair of translationally-equivalent molecules. Because the transition dipole of BP-DPP points in the direction of the intermolecular hydrogen bond, the  $\text{NH}\cdots\text{O}$  hydrogen bond serves to align the transition dipoles in a fashion “head-to-tail”, giving a large bathochromic shift of about  $2900 \text{ cm}^{-1}$ . On the other hand, the molecule pairs ①  $\sqrt{}$  and ①  $\infty$  are arranged in a “parallel” fashion and lead to a hypsochromic shift of about  $1750 \text{ cm}^{-1}$ . As for the translationally-inequivalent molecules, there are four diagonal pairs: ①  $\approx$ , ①  $\Delta$ , ①  $\geq$ , and ①  $\textcircled{9}$ . The angle of these pairs are below the critical angle of  $54.7^\circ$ , so that these pairs displace the absorption band toward longer wavelengths by about  $2500\text{--}2650 \text{ cm}^{-1}$ . In total, both hydrogen bond pairs and diagonal pairs are found to greatly contribute to the bathochromic shift. In particular, the diagonal pairs that are specific to the “bricks in a brick wall” structure are effective in displacing the absorption band toward longer wavelengths. This type of the diagonal contribution is not found in other DPP derivatives,<sup>8</sup> although the contribution due to the hydrogen bond pair appears in common in all DPP derivatives. This explains that the “bricks in a brick wall” structure is responsible for the bathochromically displaced absorption band of BP-DPP that yields its bluish red color.

### Temperature Dependence of the Absorption Spectrum of Evaporated BP-DPP

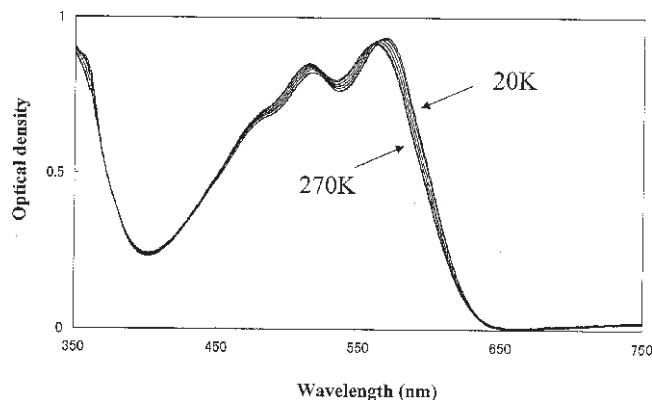
The extent of the spectral shift as caused by exciton coupling effects depends largely on the molecular arrangement. Because the intermolecular interactions are supposed to be enhanced due to lattice contraction at low temperatures, temperature dependence of absorption spectra is a good measure for the characterization of the electronic transition associated with molecular arrangement.

Figure 5 shows the temperature dependence of evaporated BP-DPP whose crystalline phase was identified as the same phase as that of the single crystal. The absorption spectrum exhibits a significant tem-

**TABLE III.** Spectral Displacements of BP-DPP Due to Exciton Coupling Effects

Molecule pair	No. of equivalent molecule	$r(\text{\AA})$	$\theta(^{\circ})$	$\Delta E (\text{cm}^{-1})$
1. Translationally-equivalent pairs				
① and ②, ① and ③	2	7.23	2.17	–2880
① and ②, ① and $\infty$	2	6.79	89.89	1737
2. Translationally-inequivalent pairs				
① and $\approx$	1	4.82	44.09	–2657
① and $\Delta$	1	4.96	42.80	–2740
① and $\geq$	1	4.98	43.75	–2500
① and $\textcircled{9}$	1	5.08	42.52	–2614
$\mu = 2.17$				





**Figure 5.** Temperature dependence of the absorption spectra of evaporated BP-DPP measured in the range between 20 and 270 K in increments of 50 K.

perature dependence, showing a slight further bathochromic shift on lowering the temperature. This indicates that the absorption band is very structure-sensitive and is due to intermolecular interactions. In other words, the absorption band is correlated with molecular arrangement.

### Conclusions

The electronic structure of BP-DPP in the solid state has been studied on the basis of the crystal structure and intermolecular interactions. The following conclusions can be drawn from the present investigation:

1. The crystal structure of BP-DPP revealed that the molecules constitute a two-dimensional  $\text{NH}\cdots\text{O}$  hydrogen-bond network on the molecular plane and that the molecules are arranged in a fashion "bricks in a brick wall" along the stacking axis.
2. The hydrogen bond serves to align the transition dipoles "head-to-tail", leading to a large bathochromic shift of the absorption band. In addition, the diagonal pairs that are specific to the brick wall structure are found to greatly displace the absorption band toward longer wavelengths. The above double effect explains why the absorption band of BP-DPP is positioned at a longer wavelength compared with ordinary DPP pigments.

3. The BP-DPP molecule is deformed on going from solution to the solid state, giving rise to a modest dipole moment in the solid state. The appearance of the dipole moment upon crystallization seems to be prerequisite for the formation of the brick wall structure.  $\blacktriangle$

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