J-aggregate-Like Structure and its Influence on the Electronic Spectra in 1,4-diketo-3,6-bis(4-biphenylyl)pyrrolo[3,4-c]pyrrole

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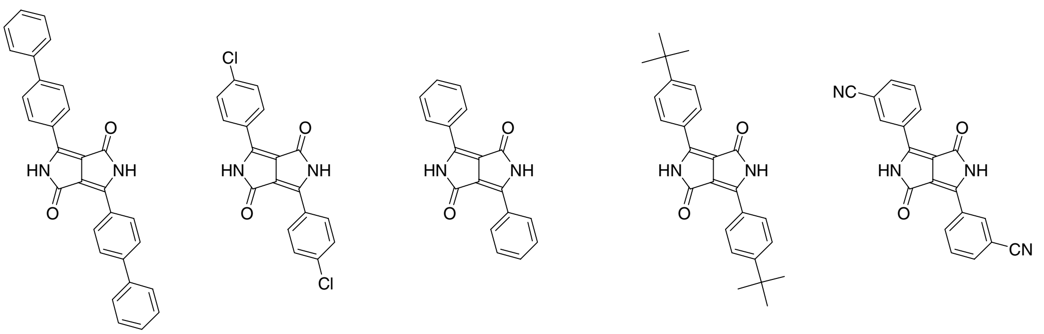
Abstract

The title compound (BP-DPP), an industrially important red pigment, 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 a fashion "bricks in a brick wall", 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. Additionally, there are diagonal pairs of the brick wall structure whose exciton coupling again induces a bathochromic shift. Both the hydrogen bond on the molecular plane and the brick wall structure along the molecular stack are found to significantly displace the absorption band toward longer wavelengths on going from solution to the solid state.



BP-DPP p-Cl DPP DPP TB-DPP *m*-CN DPP

bluish red vivid red yellowish red

Figure 1. DPP pigments and their colors.

Introduction

Diketopyrrolopyrrole (abbreviated to DPP) pigments are industrially important red pigments based on the novel diketopyrrolopyrrole chromophore.[1] DPPs are also used as colorants for imaging areas as well as a color filter for LCD applications. Up to now, five DPP-derivatives are on the market (Fig.1) and most of their structures have already been analyzed: *p*-Cl DPP[2], DPP[3], TB-DPP[4] and *m*-CN DPP[5]. Although the absorption spectra of these derivatives are not so different in solution, the colors in the solid state are strikingly different, 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 yellowish component. The correlation between the crystal and electronic structures of DPP pigments, except for BP-DPP, has already been discussed in our previous paper from the stand point of crystal structure and exciton coupling effects.[6] The results are fully consistent with experiment.[7,8]

On the other hand, the title compound (1,4-diketo-3,6-bis(4-biphenylyl)pyrrolo-[3,4-c]pyrrole; BP-DPP) exhibits a shade of bluish red and gives the longest-wavelength absorption band (*ca* 560 nm) among DPP pigments.

The purpose of the present investigation is to analyze the crystal structure of BP-DPP and clarify its electronic structure.

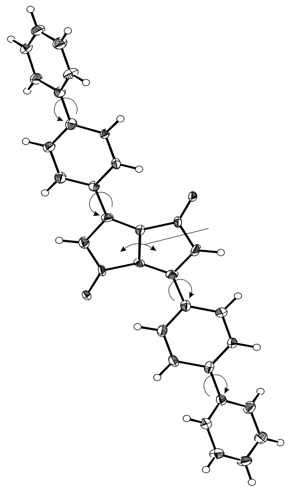


Figure 2. Molecular conformation of BP-DPP.

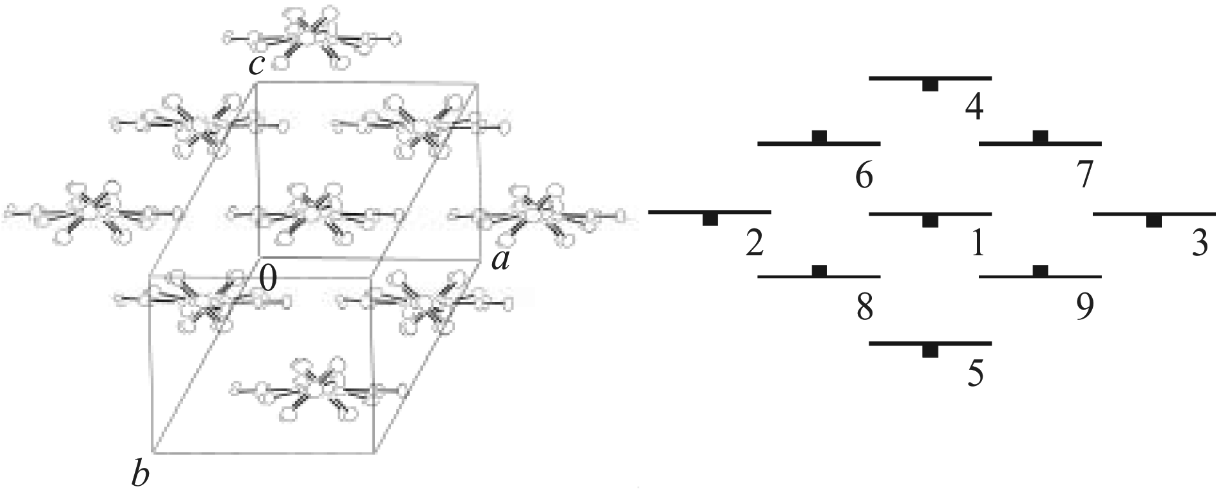


Figure 3. Molecular arrangement of BP-DPP: (a) crystal structure and (b) schematic view.

Results and Discussion

Crystal Structure

The crystal data of BP-DPP are: triclinic, P-1, Z=2, a=7.221(1), b=21.834(4), c=6.774(1) Å, α=95016(1), β=90.08(1), γ=93.83(1)°. Fig.2 shows the molecular conformation of BP-DPP. The molecule is deformed as characterized by molecular symmetry of 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 175.61°. Due to this deformed structure, a dipole moment of 0.16 D appears perpendicular to the molecular plane as calculated by MOPAC93.[9]

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 a fashion "bricks in a brick wall", just like J-aggregates in cyanine dyestuffs.[10] There are two kinds of stacking columns: one is composed of the molecules with an upward dipole moment while the neighboring column comprises the molecules with a downward dipole moment. The polar molecules are stacked pairwise so as to reduce the electrostatic energy.

On the other hand, on 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.[2-5]

Polarized Reflection Spectra

Figure 4 shows the polarized reflection spectra measured on the (0-10) 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 to be noted that the two visible bands and the reflection shoulder appear and disappear simultaneously by 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, and the second-longest band (520 nm) to the 0-1 and the reflection shoulder (475 nm) to the 0-2. It is also evident from the present polarization experiment 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. [6,8]

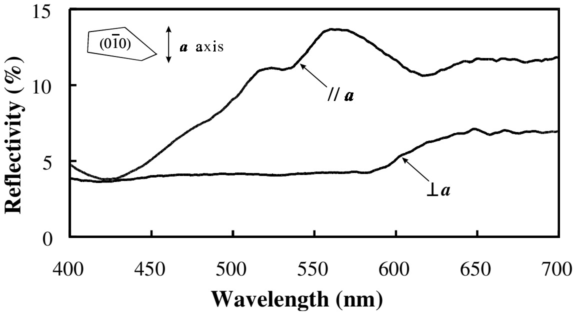


Figure 4. Polarized reflection spectra measured on the (010) plane of BP-DPP single crystals.

Spectral Displacements Due To Interactions Between Transition Dipoles

Since the absorption coefficient of BP-DPP (that is proportional to the square of the transition dipole) is quite large (*ca* 3.71×104 cm^{-1} in dimethylsufoxide), it is likely that the interaction between transition dipoles ("exciton coupling") will occur in the solid state. This may lead to a 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[11]: $\Delta E_{\text{exciton}} = |\mu|^2 (1\text{-}3\cos^2\theta) / r^3$, where μ denotes the transition dipole, r and θ the distance and angle between two transition dipoles. The term ($1\text{-}3\cos^2\theta$) determines the direction of the spectral shift. The bathochromic or hypsochromic shift depends on the critical angle of $\theta = 54.7°$, 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 θ were directly obtained from the crystal structure. The transition dipole μ was calculated on the basis of the X-ray x, y, z coordinate sets using the INDO/S Hamiltonian.12

The results are given in Table 1. The numbering of the molecules in Table 1 corresponds to that in Fig.3(b). Of 14 nearest-neighbor molecules around molecule 1, eight major molecules numbered 2 to 9 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 as characterized by translationally-equivalent molecules. Since the transition dipole of BP-DPP points the direction of the intermolecular hydrogen bond, the NH…O hydrogen bond serves to align the transition dipoles in a fashion "head-to-tail", giving a large bathochromic shift of about 3000 cm-1. On the other hand, the molecule pairs 1&4 and 1&5 are arranged in a fashion "parallel" and lead to a hypsochromic shift of about 1800 cm-1. As for the translationally-inequivalent molecules, there are four diagonal pairs: 1&6, 1&7, 1&8 and 1&9. The angle of these pairs are below the critical angle of 54.7°, so that these pairs displace the absorption band toward longer wavelengths by about 2000-3500 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 of 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,6 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 bathchoromically-displaced absorption band of BP-DPP which give a bluish red color.

Table 1. Spectral displacements of BP-DPP due to exciton coupling effects.

Molecule pair	No. of equiv. molecle	r (Å)	θ (°)	ΔE(cm^{-1})
Translationally-equivalentpair				
1&2, 1&3	2	7.22	2.74	-2936
1&4, 1&5	2	6.77	87.95	1777
Translationally-inequivalent pair				
1&6	1	5.08	41.26	-2947
1&7	1	4.96	46.75	-1860
1&8	1	4.96	43.86	-2550
1&9	1	4.82	40.97	-3520

$\mu = 2.19$

Conclusions

The electronic structure of BP-DPP 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 NH⋯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 in a way "head-to-tail", leading to a large bathochromic shift of the absorption band. In addition, the diagonal pairs that are specific of 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 as compared with ordinary DPP pigments.
3. The BP-DPP molecule is found to be 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.

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Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi from the University of Bern in 1994. He worked in the field of organic semiconductors at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science.