Crystal structure of bis(benzylimido)perylene derivatives

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Abstract

Bis(benzylimido)perylene derivatives are organic pigments which belong to the class of perylene bisimide pigments. They show a variety of colors depending on the substituents and the molecular arrangement in the solid state. They are potentially useful as electrophotographic photoreceptors. To elucidate the reason of the high electrophotographic properties, the crystal structure of six halogenated bis(benzylimido)perylene derivatives was analyzed previously by Zugenmaier et al. and the structure-property correlation was discussed based on the crystal structure. In the present work, two new structures together with five previously determined structures have been investigated at low temperatures to gain more insight into the electrophotographic properties. The structural information is expected to give an important insight into the correlation between the structure and the electrophotographic properties of these materials.

1. Introduction

Perylene bisimide pigments (Figure 1) are widely used as colorants with high tinctorial strength in painting industries. Their colors range from red to black depending on the molecular structure, i.e., the type and nature of substituents attached on the imide nitrogen atoms and the molecular arrangement in the solid state. The correlation between the color in the solid state and the crystal structure has attracted considerable attention and has been variously discussed in the literature [1–4]. Perylene bisimide pigments also play an important role in opto-electronics industries, especially in the area of electrophotography. They are used as a photoreceptor or an electron-transporting material in light-lens photocopiers and red laser-addressed digital printers. However, the reason of the high electrophotographic properties of these molecules has not been fully clarified yet. Recently, the aggregation behavior in solution and the photosensitivity in single and dual-layered photoreceptors containing unsubstituted benzylperylene bisimide pigment has been investigated experimentally [5]. The substituent effect on the energy level of several bis(benzylimido)perylene compounds has been investigated computationally based on semiemprical molecular orbital theory [6]. Preceding this work, in order to elucidate the correlation between the crystal structure and the electrophotographic properties, the crystal structure of six halogenated benzylimidoperylene compounds was investigated at room temperature [7]. In the present work, two new structures have been clarified along with five previously determined structures which were reanalyzed at low temperatures to gain more precise geometrical parameters.

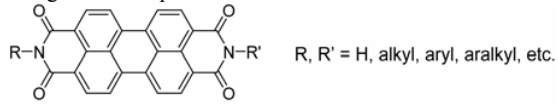

Figure 1. Molecular structure of perylene bisimide pigment.

2. Experimental Section

2-1. Sample preparation

A typical procedure for the synthesis of *N*,*N*'-bis(benzylimido)perylene derivatives is as follows [8]. To a 300 mL conical beaker, perylene tetracarboxilic acid dianhydride (0.050 mol), the corresponding benzyl amine (0.022 mol), and 200 mL of *N*-methylpyrrolidone (NMP) were added. The reaction mixture was stirred and heated on a hot plate at 200 °C for about 40 minutes. The reaction mixture was cooled to 150 °C, and was hot-filtered using a Büchner funnel with a glass fiber filter. The resultant solid in the funnel was washed first with boiling dimethyl formamide, and then several times with methanol, to give a bis(benzylimido)perylene derivative almost quantitatively. The obtained solid was pure enough for the crystal growth and used without further purification.

2-2. Measurements

Single crystal X-ray diffraction data were collected using a Rigaku R-AXIS RAPID-F two-dimensional imaging plate area detector using graphite-monochromated Cu Kα radiation (λ = 1.54187 Å) at 93 K. The intensities were corrected for Lorentz and polarization effects. The initial structures were solved by direct methods using SIR2004 [9] or SHELXS97 [10] and were refined by full-matrix least squares on $|F_o|^2$ by using SHELXL97 [11]. The absorption correction was made with ABSCOR [12]. Solid-state spectra in dispersed polyvinylacetate films were measured using a Shimadzu UV-2400 spectrophotometer. Details on the preparation of the dispersion films were reported in the literature [13].

3. Results and Discussion

3-1. Crystal structure

3-1-1. Crystallographic parameters

Table 1 details the crystallographic parameters for the seven perylene bisimide pigments investigated. In terms of the space group, four out of seven (**1**–**4**) are triclinic, two are monoclinic (**5** and **6**), whereas the last one (**7**) is orthorhombic. The lattice parameters of **1** are very similar to those of **2**, indicating these two structures are isomorphous. The same is true for **3** and **4**.

3-1-1. Bis(2-fluorobenzylimido)perylene (1)

Figure 2(a) shows the molecular conformation of **1**. The molecule is centrosymmetric. Hence, the two fluorobenzyl groups extend above and below the perylene plane. The perylene skeleton is almost planar as indicated by a small root mean square deviation of 0.020 Å from the least-squares plane. The phenyl ring of the benzyl group is also entirely planar because the r.m.s. deviation from the least-squares plane is no more than 0.005 Å. The dihedral

angle of these two least-squares planes is 86.17(7)°, indicating the benzyl group is nearly perpendicular to the perylene skeleton.

The molecules are stacked along the *a*-axis with the interplalnar distance of 3.410(3) Å and the slip angle of 33.16(16)° (Figure 2(b)). This head-to-tail arrangement of the molecules causes a bathochromic shift in the absorption spectrum due to the interactions between transition dipoles [4]. A slight overlap of π system of the perylene skeleton is observed.

3-1-2. Bis(3,4-difluorobenzylimido)perylene (2)

Figure 3(a) shows the molecular conformation of **2**. The difluorobenzyl groups are disorderd over two sites with their populations being 66% and 34%, respectively. The atoms of the major conformer is shown by an ellipsoid plot with octant shading, whereas those of the minor conformer is dipcted by open circles in Figure 3(a). The molecular arrangement of **2** is shown in Figure 3(b). The molecules are stacked with a large overlap along the *a*-axis. The interplanar distance between the molecular planes of the stacked molecules is 3.388(3) Å and the slip angle between the stacked molecules along the *a*-axis is 32.52(11)°.

The structural characteristics of **3**–**7** at low temperatures are quite similar to those at room temperature reported by Zugenmaier et al.[7] Therefore, only a brief explanation will be given below for each compound.

3-1-3. Bis(3,5-dichlorobenzylimido)perylene (3)

The molecules are stacked along the *a*-axis (Figure 4). The slip angle is 54.93(22)° and the interplanar distance is 3.426(4) Å .

3-1-4. Bis(3-chlorobenzylimido)perylene (4)

The molecules are stacked along the *a*-axis (Figure 5). The slip angle is 55.64(16)° and the interplanar distance is 3.465(3) Å .

3.1-5. Bis(3-fluorobenzylimido)perylene (5)

The molecules are stacked along the *a*-axis (Figure 6b). Since the space group of **5** is $P2_1/a$, the screw axis runs parallel to the *a*-axis. The nearest molecule along the stacking axis is therefore a transllationally inequivalent molecule as shown in Figure 6(b). The interplaner distance between the molecular plane of these molecules amouts to 3.322(2) Å. There is virtually no π-orbital overlap between the perylene skeletons of the stacking molecules.

3-1-6. Bis(3,5-difluorobenzylimido)perylene (6)

The molecules are stacked along the *b*-axis (Figure 7). The slip angle is 73.32(10)° and the interplanar distance is 3.401(2) Å .

3-1-7. Bis(4-chlorobenzylimido)perylene (7)

The crystal system is orthorhombic and the molecules are stacked along the *c*-axis (Figure 8). The nearest molecule along the stacking axis is translationally inequivalent molecule as in the case of **5**. The interplanar distance between the molecluar planes of the nearest molecule pair along the stacking axis amounts to 3.369(2) Å.

3-2. Solid-state spectra of bis(benzylimido)-perylene derivatives

Figure 9 shows the optical absorption spectra in dispersion films [13] of **1**–**7**. It should be noted that the solution spectra of these compounds (not shown here) are almost identical, indicating the benzyl substituents have almost nothing to do with the electronic structure of a single molecule. On the other hand, in the solid state, the color changes drastically depending on the molecular arrangement. This can be interpreted by the resonance interaction between transition dipoles [4].

4. Summary

Seven crystal structures of bis(benzylimido)perylene derivatives have been determined at low temperatures with high precision by single crystal X-ray analysis. The structures of **1** and **2** are isomorphous, so are those of **3** and **4**. The rest shows structural diversity. All of these structures are characterized by short interplanar distances between the molecular planes of the stacking molecules and small slip angles between the molecules along the stacking axis. These features may account for the spectral shift observed in dispersion films. The detailed investigation on the correlation between the structure and the electrophotographic properties will be the subject of a future work.

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Author Biography

Takatoshi Senju received his BSc and PhD degrees in chemistry from the University of Tokyo in 1992 and 1997, respectively. Since then he spent two and a half years in the Development and Engineering Research Center at Mitsubishi Chemical Co. in Okayama, Japan and then moved to Yokohama National University as Assistant Professor. His research interest includes synthetic organic chemistry, computational chemistry and electronic characterization of organic pigments. He is a member of the Chemical Society of Japan, the American Chemical Society, ISJ and IS&T. E-mail: tsenju@ynu.ac.jp.

Table 1 Crystallographic parameters

Compound	2-F (**1**)	3,4-F (**2**)	3,5-Cl (**3**)[a]	3-Cl (**4**)[a]	3-F (**5**)[a]	3,5-F (**6**)[a]	4-Cl (**7**)[a]
Molecular Formula	$C_{38}H_{20}F_2N_2O_4$	$C_{38}H_{18}F_4N_2O_4$	$C_{38}H_{18}Cl_4N_2O_4$	$C_{38}H_{20}Cl_2N_2O_4$	$C_{38}H_{20}F_2N_2O_4$	$C_{38}H_{18}F_4N_2O_4$	$C_{38}H_{20}Cl_2N_2O_4$
Molecular Weight	606.56	642.54	708.34	639.46	606.56	642.54	639.46
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	*P*−1	*P*−1	*P*−1	*P*−1	$P2_1/a$	*C*2/*c*	*P*bcn
Z	1	1	1	1	2	4	4
a / Å	6.4589(15)	6.7310(13)	4.1889(11)	4.1958(9)	8.3623(15)	28.687(4)	24.718(2)
b / Å	8.5739(19)	7.6986(16)	10.024(2)	9.8344(19)	11.877(2)	4.3582(7)	15.1897(14)
c / Å	13.099(3)	13.488(3)	17.404(4)	17.014(3)	13.253(2)	22.053(3)	7.2427(7)
α / °	72.634(14)	80.044(13)	104.007(16)	103.805(13)	90	90	90
β / °	77.965(15)	85.885(12)	92.509(18)	95.808(15)	104.661(12)	103.329(9)	90
γ / °	67.774(14)	73.300(13)	100.230(18)	99.710(15)	90	90	90
V / Å^3	637.1(2)	659.2(2)	694.9(3)	664.6(2)	1273.5(4)	2682.8(7)	2719.3(4)
R_1 ($F^2 > 2\sigma(F^2)$)	0.0566	0.0475	0.0574	0.0598	0.0434	0.0499	0.0397
wR_2 (all data)	0.1586	0.1560	0.2014	0.1793	0.0434	0.1529	0.1183
Goodness of fit on F^2	1.111	1.152	1.228	1.408	1.113	1.151	1.154
ρ_{min} (e Å^{-3})	0.312	0.335	0.654	0.957	0.330	0.209	0.231
ρ_{max} (e Å^{-3})	−0.286	−0.228	−0.457	−0.351	−0.236	−0.353	−0.413
d_{calc} / Mg·m^{-3}	1.581	1.619	1.693	1.598	1.582	1.591	1.562
Temperature (K)	93(2)	93(2)	93(2)	93(2)	93(2)	93(2)	93(2)
Color	pink	pink	olive green	olive green	red orange	orange	red orange

[a] Determined at 93 K. Structures at room temperature have been reported by Zugenmaier et al [7].

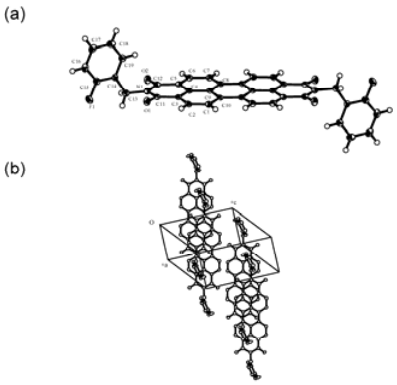

Figure 2. Bis(2-fluorobenzylimido)perylene

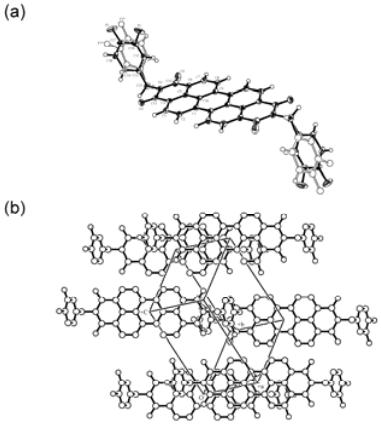

Figure 3. Bis(3,4-difluorobenzylimido)perylene. (a) Molecular conformation. The major conformer is drawn in thermal ellipsoids with octant shading along with solid bonds while the minor conformer is depicted with open circles and open bonds. (b) Molecular arrangement. Only the major conformer is shown for clarity.

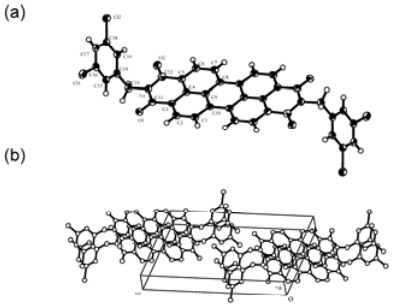

Figure 4. Bis(3,5-dichlorobenzylimido)perylene

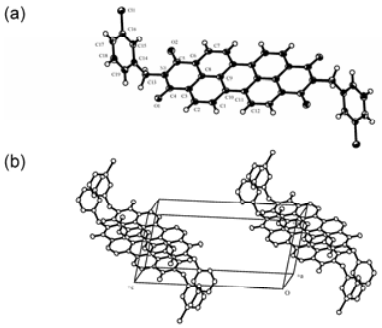

Figure 5. Bis(3-chlorobenzylimido)perylene

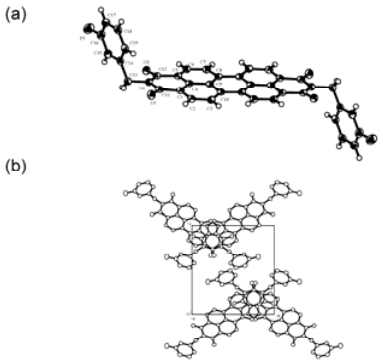

Figure 6. Bis(3-fluorobenzylimido)perylene

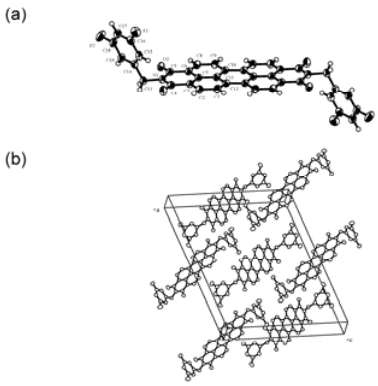

Figure 7. Bis(3,5-difluorobenzylimido)perylene

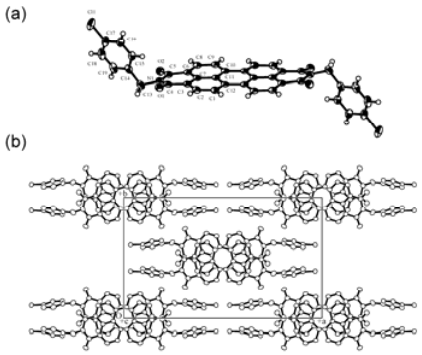

Figure 8. Bis(4-chlorobenzylimido)perylene

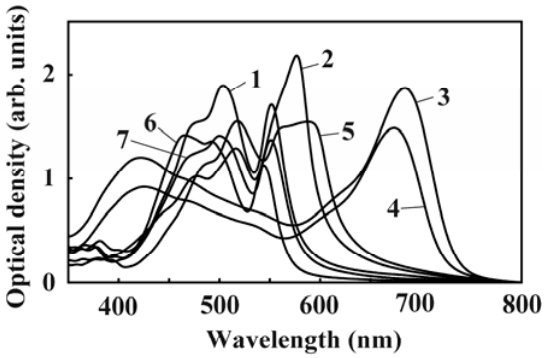

Figure 9. Visible spectra of ***1-7*** in dispersion films.