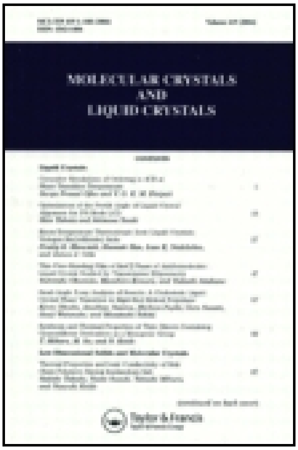

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Guest Inclusion Style of 9,10-Diphenylanthracene

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Guest Inclusion Style of 9,10-Diphenylanthracene

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9,10-Diphenylanthracene (DPA) permits the inclusion of guest molecules (hexafluorobenzene and 1,4-dioxane) by changing the arrangement of its two-dimensional layers and the size of the cavities formed by these layers in a solid state. In particular, the 1,4-dioxane guest molecules are trapped along the cavities by CH-π interactions with DPA. Crystal data for hexafluorobenzene inclusion complex in DPA, triclinic, space group $P\bar{1}$, $a = 6.118(2)$, $b = 7.571(2)$, $c = 12.982(4)$ Å, $\alpha = 78.366(4)^\circ$, $\beta = 85.001(5)^\circ$, $\gamma = 81.687(5)^\circ$, $U = 581.7(3)$ Å^3, $Z = 2$. *Crystal data for 1,4-dioxane inclusion complex in DPA, triclinic, space group* $P\bar{1}$, $a = 5.931(1)$, $b = 7.625(1)$, $c = 12.103(1)$ Å, $\alpha = 85.404(2)^\circ$, $\beta = 76.300(2)^\circ$, $\gamma = 82.909(2)^\circ$, $U = 526.96(9)$ Å^3, $Z = 2$.

Keywords: 9,10-diphenylanthracene; crystal structure; fluorescence; inclusion style

INTRODUCTION

Many solid-state organic host systems that contain guest molecules have been reported [1–5]. Recently, due to the rising demand to impart further functionality to these host systems, host systems with solid-state fluorescence have attracted considerable attention as functional

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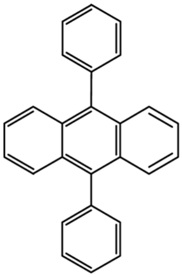
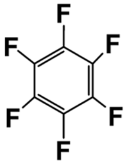
solid-state organic host systems [6–15]. In the field of photochemistry, anthracene derivatives, especially 9,10-disubstituted anthracene derivatives [16–22], are some of the most important compounds used in the design of fluorescent materials in a solution or solid state [23–28]. Among them, 9,10-diphenylanthracene (DPA) is the key skeleton of 9,10-disubstituted anthracene derivatives. However, the crystal structures of DPA systems that permit the inclusion of guest molecules are not often reported [29–31]. In particular, there is no report pertaining to the inclusion of simple guest molecules.

In this article, we report the inclusion style of simple guest molecules in DPA by using X-ray crystallographic analysis. Two types of molecules that could readily engage in π-π or CH-π interactions, hexafluorobenzene (**1**), and 1,4-dioxane (**2**), were studied.



DPA



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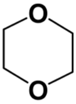

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EXPERIMENTAL

The inclusion of each type of guest molecule in DPA was achieved by the crystallization from guest solutions (2 mL) containing the particular guest molecules and DPA (10 mg, 3.0×10^{-2} mmol). Each solution was left to stand at room temperature for a few days. As a result, DPA permitted the inclusion of molecules of **1** and **2**, yielding crystals **I** and **II**, respectively [32]. X-ray diffraction data for single crystals were collected using BRUKER APEX. The crystal structures were solved by the direct method and refined by full-matrix least-squares using SHELX97. The diagrams were prepared using PLATON. Absorption corrections were performed using SADABS [33]. Nonhydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation.

RESULTS AND DISCUSSION

To understand the guest-inclusion styles of complexes **I** and **II**, X-ray analyses of these crystals were performed. The crystal structure of complex **I**, which included **1**, is shown in Fig. 1 [34].

The stoichiometry of complex **I** is DPA:**1** = 1:1 and the space group is $P\bar{1}$. Characteristically, the two-dimensional (2D) layer of DPA is formed and maintained by benzene-anthracene edge-to-face interactions (Fig. 1(a), indicated by arrow A, 2.85 Å) between the hydrogen atom at the 3-position of the phenyl ring and the anthracene ring and anthracene-benzene edge-to-face interactions (Fig. 1(a), indicated by arrow B, 2.73 Å) between the hydrogen atom at the 2-position of the anthracene ring and the phenyl ring. Two-dimensional layered

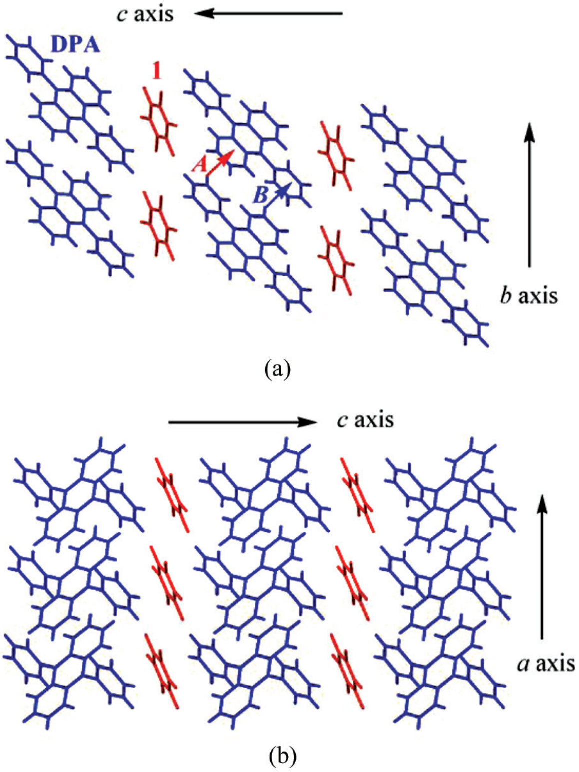


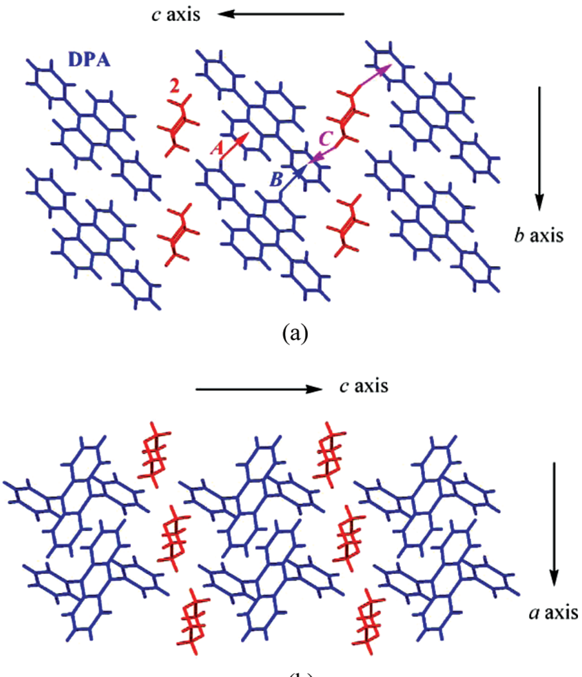
FIGURE 1 Crystal structure of complex **I**. (a) Packing structure observed along the *a* axis. Arrows A and B indicate benzene-anthracene edge-to-face and anthracene-benzene edge-to-face interactions, respectively. (b) Packing structure observed along the *b* axis.

cavities along *a* and *b* axes are formed by the 2D layer of DPA. Guest molecules of **1** are trapped along the direction of these cavities. Although the guest molecules of **1** may easily form π-π interactions with an aromatic molecule, the π-π distance between the molecules of **1** and the phenyl ring of DPA is large (4.01 Å) in this complex.

The crystal structure of complex **II**, which includes **2**, is shown in Fig. 2 [35].

The X-ray analyses revealed that the stoichiometry of this complex is the same as that of **I**, i.e., DPA:**2** = 1:1, with the same space group $P\bar{1}$. This crystal possesses a packing style of DPA that is similar to crystal **I**. DPA forms a 2D layer along the *a* and *b* axes by benzene-anthracene edge-to-face interactions (Fig. 2(a), indicated by arrow A, 2.83 Å) between the hydrogen atom at the 3-position of the phenyl ring and the anthracene ring and anthracene-benzene edge-to-face interactions (Fig. 2(a), indicated by arrow B, 2.81 Å) between the hydrogen atom at the 2-position of the anthracene ring and the phenyl ring. Molecules of **2** are trapped along the direction of the cavities formed by the 2D layers of DPA, in a similar manner as in crystal **I**. Each molecule of **2** is trapped in the 2D layered cavities by CH-π interactions between **2** and the phenyl ring of DPA (Fig. 2(a), indicated by arrow C). The CH-π distance and the angle between the C-H vector and the normal to the π-plane are 2.83 Å and 31.4°, respectively.

In complexes **I** and **II**, although the packing style of DPA is almost identical, the size of the 2D layered cavities varies slightly depending on the guest molecule. As the guest molecule changes from **1** to **2**, the interlayer distance decreases from 12.69 Å to 11.74 Å. Moreover, the average of the two torsion angles between the phenyl ring and the anthracene ring in complexes **I** and **II** increases from 69.6° to 72.8°. Comparing the crystal structures of complexes **I** and **II** with that of the previously studied DPA complex with fullerene [30], the guest-inclusion styles are common. DPA formed layered structure in all of these complexes, although the relative orientation of the host molecules in the layer was different; all the anthracene rings were parallel to each other in our complexes, while they exhibited a zigzag arrangement in the fullerene complex. DPA formed 2D cavities to accommodate the guest molecules by modifying the relative arrangement in the host layer and varying the interlayer distance. The interlayer distance in the reported complex that permitted the inclusion of fullerene was 12.57 Å, which is similar to that in complex **I**. Moreover, even in the previously reported DPA crystal without any included guest molecules [36], DPA forms a 2D layer. Although all the anthracene rings of DPA in the 2D layer structure are parallel to each other, those of DPA between adjoining 2D layers are not parallel. The interlayer distance



(a)

(b)

FIGURE 2 Crystal structure of complex **II**. (a) Packing structure observed along the *a* axis. Arrows A and B indicate benzene-anthracene edge-to-face and anthracene-benzene edge-to-face interactions, respectively. Purple arrows indicate CH-π interactions. (b) Packing structure observed along the *b* axis.

in the reported DPA crystal without guests was 6.13 Å. These results suggest that DPA permits the inclusion of guest molecules by changing the arrangement of its 2D layers and the size of the cavities formed by its 2D layers in the solid state.

9,10-Disubstituted anthracene derivative is one of the most important compounds used in the design of fluorescent materials. Therefore, in order to study the solid-state optical properties of complexes **I** and **II**, the solid-state fluorescence spectra were measured [37]. The solid-state fluorescence maxima of complexes **I** and **II** are 437 nm and 451 nm, respectively, and the shift (70 nm or 56 nm) to a lower wavelength is observed relative to the solid-state fluorescence maxima of DPA without guests (507 nm). These results indicate that this system can be used as a fluorescent host, the fluorescence of which irradiates the guest molecules.

In conclusion, the guest-inclusion style of DPA was analyzed by X-ray crystallography. In this system, 2D layers are formed by the benzene-anthracene edge-to-face and anthracene-benzene edge-to-face interactions of DPA and are altered depending on the included guest molecules. The guest molecules are trapped in the cavities formed by these 2D layers. Moreover, the solid-state fluorescence maxima of the complexes shifts to a wavelength lower than that of DPA in the solid state without any guest. It is expected that this information on guest-inclusion styles will be useful in the development of novel solid-state anthracene host systems.

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[34] Crystallographic data of **I:** $0.5C_{26}H_{18}\cdot 0.5C_6F_6$, $M = 258.23$, triclinic, space group $P\bar{1}$, $a = 6.118(2)$, $b = 7.571(2)$, $c = 12.982(4)$ Å, $\alpha = 78.366(4)$°, $\beta = 85.001(5)$°, $\gamma = 81.687(5)$°, $U = 581.7(3)$ Å^3, $Z = 2$, $D\mathrm{c} = 1.474\,\mathrm{gcm}^{-3}$, $\mu(\mathrm{Mo\ K}\alpha) = 0.118\ \mathrm{mm}^{-1}$, 5351 reflections measured, 2724 unique, final $R(F^2) = 0.0707$ using 1625 reflections with $I > 2.0\ \sigma(I)$, No. of parameters = 172, Goodness-of-fit on $F^2 = 0.993$, R(all data) = 0.1295, $T = 120(2)$ K. CCDC 667882.

[35] Crystallographic data of **II:** $0.5C_{26}H_{18}\cdot 0.5C_4O_2H_8$, $M = 209.25$, triclinic, space group $P\bar{1}$, $a = 5.931(1)$, $b = 7.625(1)$, $c = 12.103(1)$ Å, $\alpha = 85.404(2)$°, $\beta = 76.300(2)$°, $\gamma = 82.909(2)$°, $U = 526.96(9)$ Å^3, $Z = 2$, $D\mathrm{c} = 1.319\ \mathrm{gcm}^{-3}$, $\mu(\mathrm{Mo\ K}\alpha) = 0.081\ \mathrm{mm}^{-1}$, 4822 reflections measured, 2465 unique, final $R(F^2) = 0.0441$ using 2157 reflections with $I > 2.0\ \sigma(I)$, No. of parameters = 145, Goodness-of-fit on $F^2 = 1.026$, R(all data) = 0.0504, $T = 120(2)$ K. CCDC 667883. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; deposit@ccdc.cam.ac.uk).

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[37] The solid-state fluorescence maximum was measured using a C9920-02 (Hamamatsu Photonics K.K.). The excited wavelengths are 400 nm for complex **I** and DPA that includes no guest molecule and 423 nm for complex **II**.