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Correlation between Structure and Thermal Behavior in Isostructural Clathrates

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Two clathrates, (**H**)$(THF)_2$ and (**H**)$(1,3\text{-dioxolane})_2$, where **H** is 1,4-bis[3-(9-anthryl)propen-1-on-3-yl]benzene, were shown to be isomorphic by means of X-ray diffraction studies. In spite of the structural similarity, their thermal behavior was considerably different. The difference can be explained in terms of intermolecular weak forces between the host and the guest, including CH/π and O/π interactions.

Keywords: clathrate; isomorph; thermal behavior; CH/π interaction

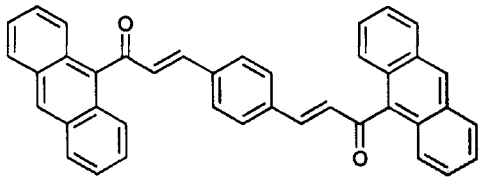
INTRODUCTION

The use of crystalline inclusion cavities as micro reaction vessels is of great interest in current chemistry,[1] and one of the central problems is to understand the correlation between structural properties of the cavity and the dynamic behavior of the molecules included in it. Ohashi and his coworkers have discussed this in terms of the volume and the shape of cavities.[2] However, recent studies on weak intermolecular forces

have indicated the importance of those interactions in dynamic behavior in crystalline state, and have prompted us to obtain a more comprehensive understanding of the correlation of structure and thermal behavior. In the present work, we have focused our attention on isomorphic crystals. They are supposed to be ideal when correlation is studied, because most of the structural features are the same in each crystals, so that different chemical and physical behavior can attribute to the distinct features directly.[3]

RESULTS AND DISCUSSION

We employed a new "wheel-and-axle"[4] molecule, 1,4-bis[3-(9-



H

anthryl)propen-1-on-3-yl]benzene (**H**) as a host, which was obtained from terephthalaldehyde and 9-acetylanthracene in moderate yield. Upon slow evaporation, **H** yielded 1:2 clathrates from tetrahydrofuran (THF) and 1,3-dioxolane solutions, as (**H**)$(THF)_2$ (**1**) and (**H**)$(1,3\text{-dioxolane})_2$ (**2**), respectively. Reflecting the similarity of both guest molecules in size and shape, X-ray structures of **1** and **2** were isomorphic (Figure 1): there exist one host and two guest molecules

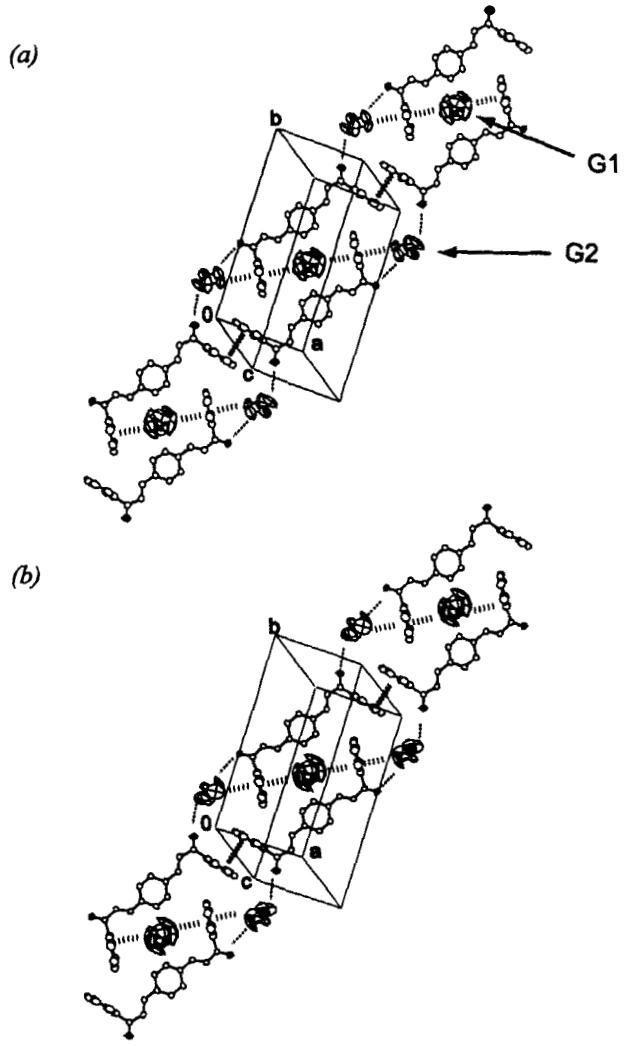


FIGURE 1 ORTEP drawing of **1** (a) and **2** (b). π/π, CH/π, and CH/O interactions are specified by wide and narrow broken, and dotted lines, respectively. Oxygen atoms are represented by discriminated ellipsoids. Hydrogen atoms are omitted for clarity.

(**G1** and **G2**) in an asymmetric unit. Two molecules of **G1** are surrounded by two host molecules, sandwiched by the π-plane of anthracene moieties. These units are stacked, having π-π interactions between anthracene planes (interplanar distances are estimated to be 3.2 and 3.4 Å for **1** and **2**, respectively). **G2**'s are accommodated in the space between stacked host molecules. It seems likely that CH/π[5] and CH/O[6] interactions are present between **G2** and **H** on the basis of their interatomic distances. It is noted that temperature factors of the guests (**G1** and **G2**) were observed to be significantly larger than those of the host, and, some of their bond lengths and bond angles were out of range of the common values. These findings indicate that both guest molecules are disordered. Accordingly, assignment of the atoms of the guest molecules was tentative in **1** and **2**.

By means of DSC (Differential Scanning Calorimetry) analyses, it was observed that **1** and **2** released both of their guest components at the same time. However, in spite of the striking similarity in molecular arrangement, their thermal stability was significantly different. Although the intrinsic boiling point of THF (65 °C) is 9 °C lower than that of 1,3-dioxolane (74 °C), **1** released its guest component at a temperature 29 °C higher than **2** (T_{onset}; **1**:116 °C, **2**:87 °C). These results can be explained as follows. As shown above, the guest THF in **1** is disordered. No matter whether the disorder is static or dynamic, two types of close contact should be present between **H** and **G1**, that is, methylene/π-plane and oxygen/π-plane. When a methylene group is directed to π-plane, an attractive CH/π interaction is yielded. On the other hand, when ethereal oxygen is located at the position nearest to

the π-plane, it should be electrostatically repelled. Although **2** is isomorphic with **1**, 1,3-dioxolane has two ethereal oxygen atoms in a molecule, so the repulsive interaction is expected to be more significant in **2**. The situation of **G2** seems more complicated because two more interactions will be present, *i.e.*, methylene/carbonyl (CH/O) and oxygen/carbonyl(O/O), which are known to be attractive and repulsive, respectively. However, it is possible to discuss the stability of **G2** in the same way as **G1**.

In the context of these studies, we have attempted to obtain clathrates of **H** and cyclopentane. Inspection of the structural and thermal data would be more instructive when the isomorphic (**H**)(cyclopentane)$_2$ is compared with **1** and **2**. But we have failed to obtain clathrates either from cyclopentane solution or from mixed solutions, probably because of the low solubility of **H** in cyclopentane.

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