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A new inclusion host: an inclusion complex between a 1,3,5-triaroylbenzene host and a benzene guest stabilized by aromatic C–H···O hydrogen bonds

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Abstract

A methoxy-functionalized C_3-symmetrical 1,3,5-triaroylbenzene derivative was prepared by cyclotrimerization of a substituted aryl ethynyl ketone. This material was found to form a stable inclusion complex with benzene in a host:guest ratio of 1:1 as revealed by X-ray crystallography. The solid state structure appears to be stabilized by aromatic C–H···O hydrogen bonds between the benzene guest and the triaroylbenzene host. © 1999 Elsevier Science Ltd. All rights reserved.

The rational design of host molecules capable of forming crystalline inclusion complexes continues to receive considerable attention.[1] Indeed, a thorough understanding of the interplay between host structure and inclusion complex formation has important ramifications in the areas of molecular recognition and crystal engineering. It is now recognized that certain structural features present in putative host compounds can maximize opportunities for inclusion complex formation.[2] Among these structural features, the overall topology of the host molecule (i.e., shape) and the presence of a rotational axis of symmetry appear to be the most important, especially in host compounds devoid of strong hydrogen bond donor and/or acceptor functional groups.[2,3]

As part of an ongoing investigation aimed at the synthesis of new molecular receptors, a study of 1,3,5-triaroylbenzene derivatives, possessing the general structure illustrated in the parent compound **1**, has been initiated. Concomitant with the initiation of this study came the realization that structures such as **1** exhibit many of the characteristics found in inclusion hosts. Specifically, **1** is a relatively large, rigid, polyaromatic compound with a rotational (C_3) symmetry axis.[4] Hence **1** and its functionalized derivatives may comprise a family of heretofore unexplored solid state host molecules.

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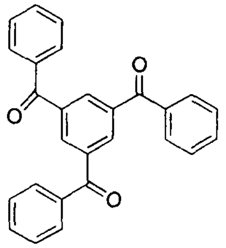

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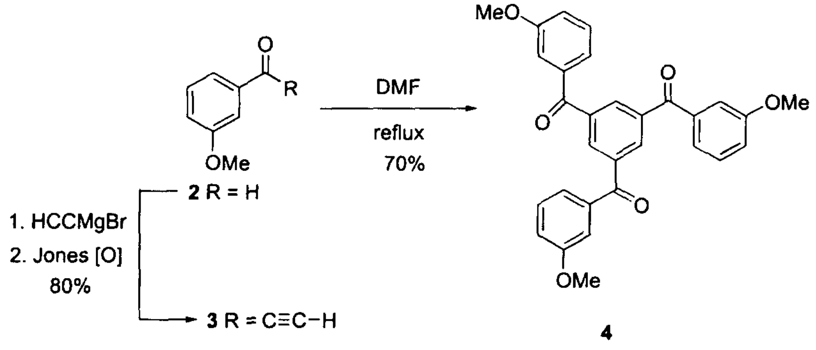
To test this theory, a functionalized 1,3,5-triaroylbenzene derivative was prepared from *m*-anisaldehyde **2** as shown in Scheme 1 (the methoxy moieties are envisioned to serve as functional group handles for further synthetic manipulation). Treatment of **2** with ethynyl magnesium bromide and oxidation of the resulting alcohol (Jones reagent) afforded aryl ethynyl ketone **3** in 80% overall yield.[5] Amine catalyzed cyclotrimerization of **3**, easily effected in refluxing dimethylformamide (DMF) according to the procedure of Balasubramanian and co-workers,[6] provided **4** as a yellow oil in 70% isolated yield.



Scheme 1.

A crystalline, stable sample of **4** was eventually obtained by slow diffusion of hexane into a benzene solution. Structural characterization of this material via single crystal X-ray diffraction did indeed reveal the presence of included guest (benzene) molecules with a host:guest stoichiometry of 1:1 (a ratio corroborated by combustion analysis).[5,7] As expected based on the symmetry present in **4**, the inclusion complex exhibits perfect C_3-symmetry in the space group P $\bar{3}$. The packing diagram of the inclusion complex viewed down the *c* axis is shown in Fig. 1. Individual molecules of **4** are stacked in columns at each corner of the unit cell and the included benzene molecules occupy voids in the lattice between adjacent columns. Furthermore, the benzene guests appear to be participating in aromatic C–H···O hydrogen bonding interactions to proximal carbonyl groups of **4** (indicated by dashed lines in Fig. 1). While the existence of C–H···O hydrogen bonds has been the subject of some controversy,[8] the aromatic H-carbonyl O distance of 2.55 Å, the nearly linear aromatic C–H···O angle of 169.4°, and the C=O···H angle of 120.9° all are consistent with the presence of hydrogen bonding interactions.[9] It is noteworthy that the C_3-symmetry inherent to **4** is relayed to the benzene guests as only the aromatic hydrogens at the 1, 3, and 5 positions are engaged in this apparent bonding. Further evidence for the integral role played by the included guests in stabilizing the solid state structure is provided by the inability to obtain solid samples of **4** in the absence of benzene.[10]

The manner in which the host molecules (**4**) attain a columnar array also is quite interesting. As shown in Fig. 2, the central aromatic rings of two molecules of **4** are overlapped (interplanar distance=4.46 Å) with one molecule rotated 60° with respect to the other. This dimeric stacking arrangement thus

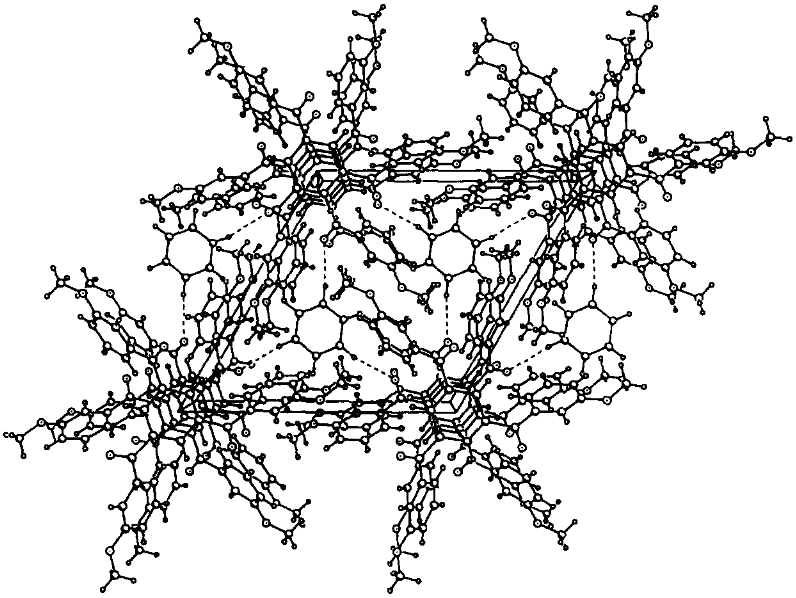


Figure 1. Packing diagram of **4**·C_6H_6

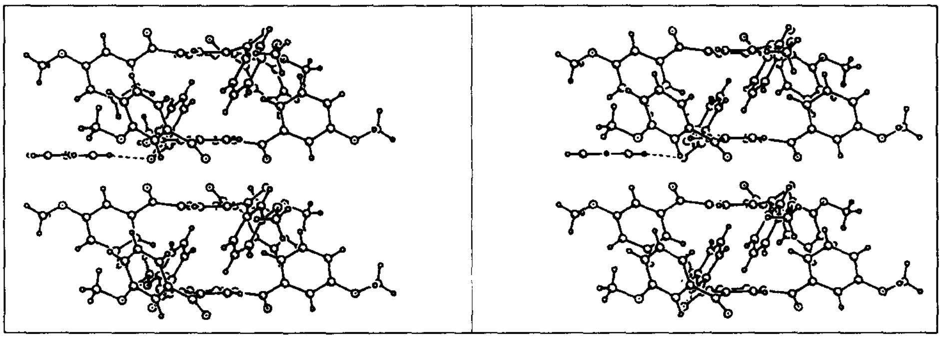


Figure 2. Stereoview of the columnar stacking arrangement in **4**·C_6H_6

allows for the interposition of the attached *m*-methoxybenzoyl substituents and this mode of packing between two host molecules is reminiscent of the 2,4,6-trisubstituted triazene 'Piedfort units' described by MacNicol.[11] Dimers of **4** are arranged on opposite sides of channels filled by carbonyl oxygen atoms. The benzene guests also occupy sites along the 'walls' of these channels.

Given the straightforward synthetic protocol available for the preparation of 1,3,5-triaroylbenzenes, it is anticipated that **4** will constitute the first member of a new family of inclusion hosts. While **4** appears to be highly selective for inclusion of benzene, systematic variation of functionality present in the triaroylbenzene framework may provide host compounds for a wide array of guests. Additionally, the C_3-symmetry present in **4** (and its congeners) is an attractive structural characteristic that potentially can be incorporated into new solution phase molecular receptors.[12] Studies along these lines are currently in progress.

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