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4-(Triphenylmethyl)benzoic acid: a Supramolecular Wheel-and-Axle Host Compound

Ram K. R. Jetti,[a] Srinivasan S. Kuduva,[a] D. Shekhar Reddy,[b] Feng Xue,[b] Thomas C. W. Mak,*[,b] Ashwini Nangia*[,a] and Gautam R. Desiraju*[,a]

a: School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
b: Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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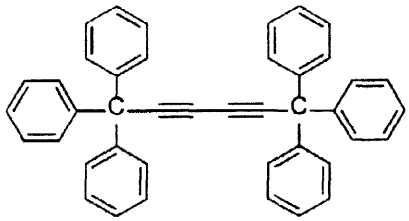
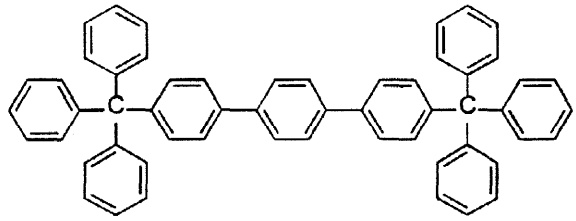
Abstract: *The title compound crystallises from several aromatic solvents to produce wheel-and-axle host-guest complexes. The crystal structures and inclusion properties of the xylene and chlorobenzene solvates are discussed.*

Wheel-and-axle compounds such as **1** contain a long, linear axis (the 'axle') that bears at both ends large, rigid substituents (the 'wheels').[1,2] Unlike most organic molecules that crystallise as single component crystals, these compounds are unable to pack properly because of their awkward shape and crystallise with the inclusion of guest molecules. Compound **1** for instance is known to form crystalline inclusion compounds with a variety of aromatic solvents.[2a]



1



2

Among the current aims of crystal engineering,[3] there is considerable interest in designing new host systems especially with a view to obtaining microporous solids.[4] In this regard, the wheel-and-axle strategy has been shown to be effective and yet the difficulties in the synthesis of appropriate molecular hosts has limited its wider application.[5] In this communication, we show that a wheel-and-axle host compound may be synthesised *supramolecularly*, thus greatly enhancing the scope of this design strategy.[6]

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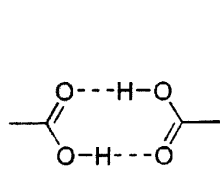
Let us consider initially the as yet unreported 4,4"-*bis*(triphenylmethyl)-1,1':4',1"-terphenyl **2** which may reasonably be expected to form inclusion compounds similar to **1**. Noting that the carboxylic acid dimer synthon **3** is the supramolecular equivalent of the 1,4-disubstituted phenyl ring,[6,7] we argued that 4-(triphenylmethyl)benzoic acid, **4** should self-assemble to yield the wheel-and-axle dimer **5**, which is the supramolecular analogue of terphenyl **2**.



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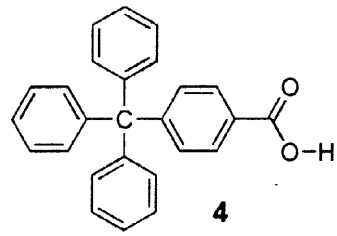

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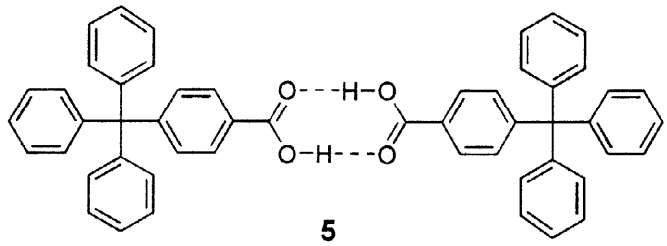
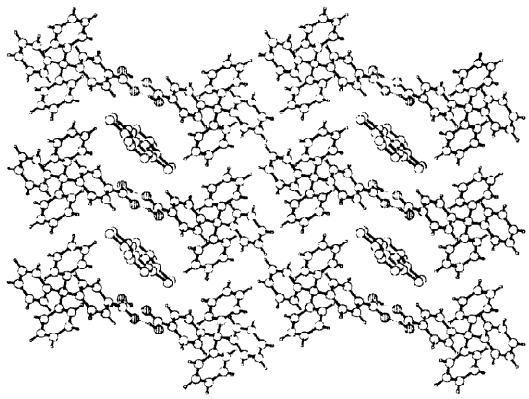
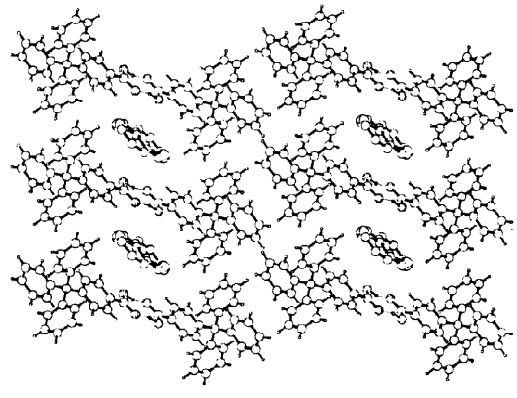


5

Our prediction was realised. Acid **4** was synthesised from 4-(triphenylmethyl)aniline ($NH_2 \rightarrow I \rightarrow CN \rightarrow CO_2H$, 35% overall yield)[8] and recrystallised from mixed xylenes to give diffraction-quality single crystals of the 2:1 acid-xylene complex. The crystal structure of **5**.xylene is shown in Figure 1a.† The acid monomers form the expected dimeric arrangement (O-H···O: D, 2.64 Å; d, 1.49 Å; θ, 167°). The packing of dimers is dominated by phenyl···phenyl interactions[9] and this leads to the creation of voids that are occupied by disordered xylene molecules. The model for least-squares refinement assumes partial occupancies of each of the three isomeric xylenes because ^1H NMR integration shows that the crystals contain approximately equal amounts of the three.



a



b

Figure 1: Crystal structure of **5**.xylene (a) and **5**.PhCl (b) down [100] showing the supramolecular axle and the disordered solvent molecules. Oxygen atoms are shaded and hydrogen bonds are shown as dotted lines.

It was further observed that acid **4** incorporates a number of other aromatic solvents in its crystals. These include each of the pure xylenes but curiously, the crystals from *p*-xylene were not as large or well formed as those obtained from the xylene mixture. Crystals that contain ethylbenzene, mesitylene, chlorobenzene and toluene, but not benzene, were also obtained. Of these, the crystals from chlorobenzene were of diffraction quality and the expected 2:1 adduct was indeed formed. The crystal structure of **5**.PhCl† (Figure 1b) is isostructural to **5**.xylene and contains disordered chlorobenzene molecules in the voids created

by the close-packed triphenylmethyl groups. In each host-guest crystal, the extent of solvent incorporation and the stability at ambient temperature with respect to guest loss was monitored by NMR. In every case, save toluene, the crystals incorporated a stoichiometric amount of solvent (2:1) and this was retained indefinitely. The toluene adduct completely lost its guest component under ambient conditions in less than a week. Presumably the size of the host cavity formed is just sufficient for a snug fit of xylene, ethylbenzene or mesitylene and, as such, is too large for toluene and benzene thereby permitting their easy escape and/or non-inclusion.

Differential scanning calorimetry showed loss of xylene and chlorobenzene from the respective solvates of **5** at 120 and 114 °C, followed by the melting endotherm at 262 °C of the unsolvated material. Inspection of Figure 1 suggests that escape of the solvent channel should be most facile along the [100] direction of the crystal. When the needle-like crystals were heated slowly on a hot-stage microscope, a frontal migration along [100] occurred between 80-100 °C over 5 min corresponding to solvent loss. This is illustrated in Figure 2 for **5**.xylene. Crystal simulations (Cerius^2)[10] of the xylene and chlorobenzene complexes of **2** also showed that these putative structures are similar to the observed structures of the supramolecular host **5** with the same solvents. This suggests that the wheel-and-axle host-guest complexes with a supramolecular axle behave analogously to their molecular siblings.[1,2] In this regard, our results are of significance because the synthesis of terphenyl **2** is expected to be both difficult and long.[11]

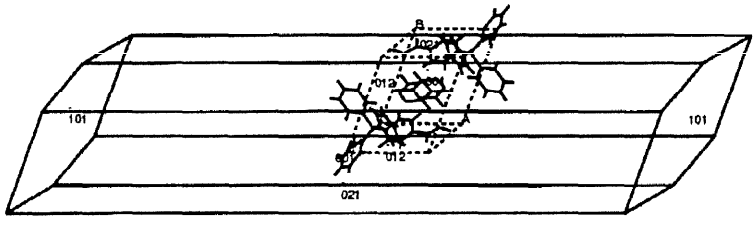


Figure 2: Morphology of **5**.xylene to show the loss of guest solvent along [100]. The crystal morphology was generated with the Dreiding 2.21 force field in the Cerius^2 program[10]

A search of the Cambridge Structural Database[12] revealed another compound with similar features. In the EtOH clathrate of 9-phenylfluorene-9-carboxylic acid (refcode JIDCEE)[13] the solvent molecules interrupt the hydrogen bonding pattern of the carboxylic acid group forming a rather bloated axle, the visualisation of which is somewhat subjective. In contrast, however, the title compound **5** provides a clear and unambiguous demonstration of the supramolecular wheel-and-axle principle.

This work demonstrates that: (1) the supramolecular nature of host **5** does not diminish its ability to include and retain appropriate guest molecules; (2) the host behaviour is general as demonstrated by the incorporation of many aromatic solvents with the same stoichiometry and by the isostructurality of the xylene and chlorobenzene complexes; (3) a supramolecular axle does not seem to be particularly flimsy when compared to a conventional molecular axle. In summary, it may be noted that the concepts of supramolecular synthesis[14] can be used in conjunction with molecular synthesis to gain rapid and convenient access to systems and functions that are often obtained only with difficulty and tediousness with molecular synthesis alone.

Acknowledgements

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† *Crystal structure data:* **5**.xylene: $(C_{26}H_{20}O_2)$. $0.5(C_8H_{10})$, triclinic, $P\bar{1}$, a = 7.327(1), b = 9.042(2), c = 18.534(4) Å, α = 88.09(3), β = 85.07(3), γ = 68.07(3)°, V = 1134.8 (4) Å^3, ρ_c = 1.1896 g cm^{-3}, Z = 2, 2351 reflections, 290 parameters, R = 0.0660, the model assumes the presence of *p*-and *m*-xylene in a 1:2 ratio and this effectively mimics the presence of *o*-xylene also. **5**.PhCl: $(C_{26}H_{20}O_2)$. $0.5(C_6H_5Cl)$, triclinic, $P\bar{1}$, a = 7.310(1), b = 8.994(1), c = 18.454(2) Å, α = 89.19(1), β = 85.75(1), γ = 68.23(1)°, V = 1123.5(2) Å^3, ρ_c = 1.21 g cm^{-3}, Z = 2, 2212 reflections, 270 parameters, R = 0.0755. For both crystal structures, all non-hydrogen atoms of the acid molecule were refined anisotropically and all non-hydrogen atoms of the solvent were treated isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.