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The first example of a crystalline guest-free form of the tris(5-acetyl-3-thienyl)methane (TATM) host material†

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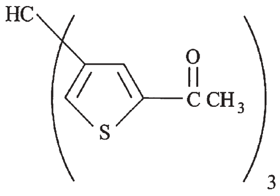
The first example of a guest-free crystalline form of tris(5-acetyl-3-thienyl)methane (TATM), in both powder and single crystal form, was obtained by leaching water-soluble guests out of the guest–host inclusion compounds with acetone, ethanol and methanol.

Tripodal host molecules form a versatile class of supramolecular materials which include triphenylmethane[1,2] and analogues, such as TATM[3–8] (**1**). So far, an unsuitable potential guest has yet to be encountered for this host.[4] TATM guest–host materials show a wide variety of stoichiometries and structural motifs,[5,6,8] and they have also demonstrated some propensity for polymorphism.[5g,8a] Indeed, a recent study culminated in the discovery of five different forms of the 2 : 1 host : guest compound of TATM with 1,3-dichloropropane.[8c] What is puzzling about TATM is that a crystalline guest-free form of the pure host has yet to be reported. Upon heating or vacuum sublimation of TATM inclusion compounds, the product host material is an amorphous solid, melting at 45–50 °C. It is likely that the difficulty in producing a crystalline guest-free material and the propensity for polymorphism have similar bases: it is clear that the TATM molecules lack the ability to interact with each other *via* strong directional interactions. The absence of strongly preferred orientations of the thienyl rings is likely to give a variety of conformational isomers in the liquid or vapour, thus making efficient packing difficult upon solidification. In almost all structural studies, the host and guest generally interact very weakly through van der Waals forces, so the guest appears to play a key role in directing the solid inclusion compound to a structure that packs efficiently.



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Crystals of the guest-free host suitable for single-crystal X-ray analysis were prepared by layering distilled water over a batch of methanol/TATM crystals in a small vial. The vial was then closed and placed in an oven at 70 °C for about 2 weeks. The bulk product was prepared by heating a TATM inclusion compound in hot water (≈70 °C), with stirring, for about one week. TGA and ^{1}H solution NMR experiments both conclusively show that the product is practically guest-free. Powder X-ray diffraction and ^{13}C CP/MAS solid-state NMR were used for bulk phase identification, and indicated that the four bulk powder products (the ethanol-, methanol-, acetone- inclusions and the guest-free TATM host), were identical to their respective single crystals, with consistent results from PXRD and single crystal diffraction measurements. The data for products obtained from both bulk phase techniques showed that the same guest-free lattice was obtained, regardless of the starting material. The spectra of the guest free products show sharp signals, attesting to a crystalline material. On the other hand, vacuum sublimed (amorphous) guest-free TATM gave broad signals for both NMR and PXRD data sets, suggesting a broad distribution of electronic environments.

The crystal structures of the three starting materials were determined by single-crystal X-ray diffraction.‡ All three compounds were isostructural, space group $P\bar{1}$, with one TATM molecule and half of a guest molecule in the asymmetric unit. The room temperature structure of the TATM/ethanol inclusion compound has been previously reported.[5c] The present study, at 125 K, resolves guest disorder in the methanol (63 : 37) and the ethanol (55 : 45) inclusions. In all three compounds the guests are also disordered across an inversion center. One of the guest-free single crystals that were screened prior to structural analysis was found to have almost the same unit cell parameters as its starting material (TATM/methanol). Structural analysis revealed that although the TATM framework was indeed isostructural to the starting material, when the disordered guest was modeled as methanol partially occupying the guest site, ≈90% of the guest cages were guest-free.

The asymmetric unit of the guest-free compound is shown in Fig. 1. The structure is triclinic, space group $P\bar{1}$ with two crystallographically distinct TATM molecules. The TATM molecules appear to be arranged in bilayers stabilized by quartets of π-stacked thienyl rings. If we label the thienyl rings from the number of the carbon atom that is bonded to the methine carbons (C1 and C1′) then rings 8 and 14′ (ring separation, $d \approx 3.7$ Å) are π-stacked (Fig. 1). In addition, thienyl ring 8′ and 14 in Fig. 1 appear to weakly π-stack with rings 14 and 8′ respectively ($d \approx 4.4$ Å) with equivalent TATM molecules in adjacent unit cells to produce ribbons of π-coupled TATM molecules extending along the ***a*** direction. The ribbons are arranged in layers in the ***ab*** plane. Adjacent layers interdigitate forming bilayers (fig. 2). It appears that additional π stacking between rings 8 and 8 ($d \approx 3.8$ Å) and 8′ and 8′ ($d \approx 4.0$ Å) stabilize this packing motif. As a result two distinct quartets of π-stacked rings, 14-8′-8′-14 and 14′-8-8-14′ are

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† Electronic supplementary information (ESI) available: CIF files for the starting materials, 90% depleted (MeOH) and guest-free compounds. See http://www.rsc.org/suppdata/cc/b4/b417110a/
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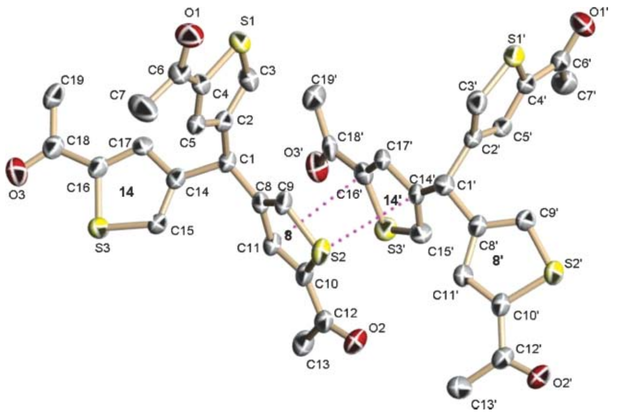

Fig. 1 Ortep plot of the asymmetric unit of guest-free TATM. The dotted lines indicate π–π stacking between thienyl rings **8** and **14′**.

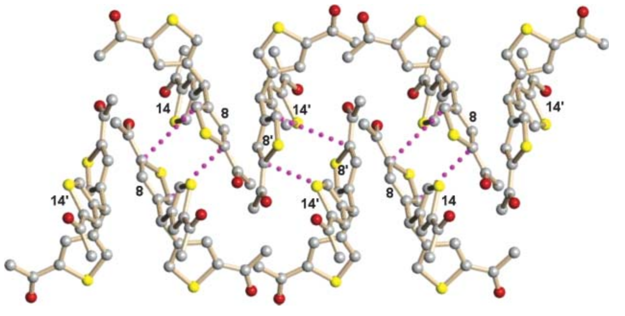

Fig. 2 View down the ***a*** axis showing the bilayer packing motif. The ***b*** axis is horizontal. The dotted lines denote π–π interactions between the layers.

observed within the bilayer. Adjacent bilayers interact through van der Waals and C–H···O contacts.

The host torsion angles of the thienyl rings about the central methine C–H bond for the three starting materials are very similar both to each other and also to Herbstein's groups I, II and IV, namely the ethyl acetate, cyclohexane **A** and *n*-hexane inclusions respectively.[9] However, the guest-free host torsion angles appear to be unique. The averages for the two independent host molecules are −18.68 (±1.44), 113.65 (±3.40) and 126.37° (±0.73°).

For all three starting materials, there is a considerable increase in polycrystalline density (He pycnometry) on going from the starting material (avg 1.338(6) g cm^{-3}) to the guest-free product (avg 1.377(3) g cm^{-3}), suggestive of more extensive attractive intermolecular interactions in the crystalline guest-free material, when compared to their respective starting materials. Vacuum sublimed guest-free TATM has a significantly lower density, 1.348(1) g cm^{-3}, suggestive of weaker intermolecular interactions. A correlation may also be made with the DSC results, where, for the three starting materials, the order of polycrystalline density (acetone > ethanol > methanol) is the same as the order of both the melting temperature and the enthalpy of decomposition.

We were also able to correlate thermal stability (*i.e.* melting point) with residual guest content for the three guest free materials. When the guest-free product has a greater residual guest content, namely from the ethanol and methanol inclusions (0.17% (each) by mass), it has a lower melting point (120.20 and 125.39 °C, respectively) when compared to the guest-free material with a lower residual guest content, namely prepared from the acetone inclusion, which has a higher melting point (0.042% by mass, T_m = 128.76 °C). The residual guest content, which presumably is an impurity in the guest-free lattice, was measured by solution ^{1}H NMR.

We now consider the mechanism by which the guest-free form is produced. One possibility is a layer-by-layer conversion of particles from the outside in as guest is leached out, with the inclusion crystal acting as a template. However, the observation of a crystal with 10% occupied guest sites suggests otherwise. The crystal must have considerable stability up to minimum site occupancy. At a critical minimum concentration of guest, the crystal converts to the guest-free form, and this seems to be possible as a single-crystal-to-single-crystal transition. The residual guest in the new crystal must then be part of the sub-minimal concentration that is trapped interstitially, perhaps between the host bilayers.

Finally, we attempted to incorporate guests into guest-free TATM from the vapour phase. As judged by ^{1}H solution NMR, acetone vapour entered and transformed the guest-free TATM lattice, whereas methanol and ethanol vapour did not. We then incorporated two more volatile guests, namely methylene chloride and bromoethane. Of the three solvent vapours that entered the guest-free host lattice, PXRD and ^{13}C CP/MAS NMR measurements revealed that acetone and methylene chloride formed TATM inclusion compounds identical to those formed by recrystallization from solution, while bromoethane formed an as yet unidentified crystalline phase.

In this communication, we have presented a technique for preparing a crystalline guest-free form of TATM. We found that the same guest-free lattice resulted regardless of the starting material, however all three starting materials are isostructural. It remains to be seen whether a different guest-free lattice (polymorph) can be obtained from a TATM inclusion compound starting material that is from a different structural family (*e.g.* benzene/TATM or carbon tetrachloride/TATM). We are presently performing such experiments.

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Notes and references

‡ Single crystal X-ray diffraction data were measured on a Bruker SMART diffractometer equipped with a CCD detector, using Mo Kα radiation (λ = 0.71073 Å) in the ω scan mode. The acquisition temperatures were either 125 (starting materials) or 173 K (guest-free). The data reduction included corrections for Lorentz and polarization effects. The crystal structures were solved by direct methods and refined by full-matrix least-squares routines using the SHELXTL program.[10] A multiscan absorption correction was made with SADABS software.[11] Direct methods yielded all non-hydrogen host atoms in the unit cell, and all non-hydrogen atoms were refined anisotropically. The host hydrogen atoms were located in the difference Fourier map, while the guest hydrogens were placed in calculated positions with a riding temperature factor and bond length constraints. Since all three starting materials and the partially-occupied methanol inclusion are isostructural to each other and also to at least five previously reported structures, their crystal data are included in the supplementary

material. For guest-free TATM, the crystal system is triclinic $P\bar{1}$, $a = 10.500(1)$, $b = 12.530(1)$, $c = 14.835(2)$ Å, $\alpha = 82.32(1)$, $\beta = 72.31(1)$, $\gamma = 88.53(1)^\circ$, $V = 1842.7(4)$ Å^3, $Z = 2$, $F(000) = 808$, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0676$, $wR_2 = 0.1626$ (16789 reflections total, 6508 unique). CCDC 255669–255673. See http://www.rsc.org/suppdata/cc/b4/b417110a/ for crystallographic data in .cif or other electronic format.

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