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Polymorphism and Structure in a Pentamorphic Guest–Host Material: The Tris(5-acetyl-3-thienyl) Methane (TATM) Inclusion Compound with 1,3-Dichloropropane

Paul S. Sidhu,^{*,‡} Gary D. Enright,^{*,†} Konstantin A. Udachin,[†] and John A. Ripmeester^{*,†,‡}

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6, and Department of Chemistry, Ottawa-Carleton Chemistry Institute, Carleton Campus, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

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ABSTRACT: In this work, we describe the preparation and structural properties of five polymorphs of the 1G:2H, 1,3-dichloropropane/tris (5-acetyl-3-thienyl) methane (TATM) inclusion compound. A number of different preparative methods were used to give products whose structures were solved by single-crystal X-ray diffraction. In addition, solid-state ¹³C NMR spectroscopy and powder X-ray diffraction (PXRD) were used for bulk phase identification. On the basis of the unit cell parameters determined from single crystal X-ray diffraction experiments, the PXRD results were used to resolve the products as being from either pure or mixed phases. In four of the five forms, the host TATM molecules have similar torsional conformations and share a common layered motif. The guest molecules are disordered and reside in cages or channels that are formed from the stacking of these layers. In the fifth form, the conformation of the TATM host molecules differ significantly, and the disordered guests reside in a pronounced zigzag channel. Apparently, slightly different conformations for the host and the flexible guest give structures that differ little in energy. The results suggest that minor changes in synthetic procedures can have a profound effect on the structure of the resulting crystalline product. Some of the structures presented here are closely related to other structures previously reported for TATM inclusion compounds with a variety of guests, suggesting that this may be a particularly rich area for studying polymorphism.

Introduction

Tris (5-acetyl-3-thienyl) methane (TATM), **1**, is a much-studied tripodal host molecule^{1–6} structurally related to the triphenylmethane group of hosts.⁷ In a preliminary study,² inclusion compounds resulted for every solvent from which the host was crystallized. TATM guest–host materials show a variety of stoichiometries and structural motifs.^{3,4,6} Somewhat surpris-

ingly, only three general distinct conformations of the substituted thienyl rings have been encountered among the reported structures.⁸ Upon guest removal by vacuum sublimation, the host material becomes an amorphous solid, which has a broad melting point range of 50–58 °C. So far, a crystalline form of the guest-free host material has yet to be reported. Likely reasons are that

the host molecules lack the ability to interact with each other via strong directional interactions, as there are only acetyl oxygens and weakly acidic hydrogens. In addition, despite the small number of observed conformations in the solid state,⁸ it is likely that a wide variety of conformational isomers are present in the liquid and vapor, thus making efficient packing difficult upon solidification.

For these reasons, molecules such as TATM may well be good candidates for finding multiple polymorphic forms, and indeed for two guests dimorphs are known.^{4f,6a} It is widely accepted that polymorphism provides a unique opportunity to study the effects of molecular structure upon bulk properties,^{9–13} conformational preferences,^{14–16} the ability to influence the crystallization process,^{17–20} and crystal engineering applications.^{21,22}

As dimorphic forms have previously been encountered, it is apparent that in any investigation of TATM guest–host materials, it is important to verify that the bulk crystalline product is indeed characteristic of that obtained from single-crystal X-ray diffraction analysis. During the course of such an investigation, it was discovered that a variety of crystal forms could be obtained with 1,3-dichloropropane as guest. Ultimately, five different crystal forms were identified for the 2:1 host/guest compound that were sufficiently stable to study their structural properties in detail. This level of polymorphism is unusual, as evident from several surveys: for compounds containing C, H, N, O, F, Cl, and S, there were 291 dimorphic compounds, 27 trimor-

* To whom correspondence should be addressed. Phone: (613) 993-2011. Fax: (613) 998-7833. E-mail: john.ripmeester@nrc-cnrc.gc.ca; gary.enright@nrc-cnrc.gc.ca.

[†] National Research Council of Canada.

[‡] Ottawa-Carleton Chemistry Institute.

phic, 3 were tetramorphic, while one of the survey papers reported a hexamorphic system.²³

Experimental Procedures

TATM was prepared according to literature methods^{1,5} from commercially available reagents (Aldrich). When it became apparent that multiple forms of the 1,3-dichloropropane/TATM inclusion compound existed, six different techniques were used to prepare either single crystals or polycrystalline powders of the 1,3-dichloropropane/TATM inclusion compound as follows:

(A) Anneal 50 °C: Dissolve 500 mg TATM in 2 mL of 1,3-dichloropropane, seal in a 20 mL screw cap vial, place in an oven at 50 °C, and allow to anneal for 2 weeks, then cool to room temperature at a rate of 5 °C per day.

(B) Fast cooling: Seal same mixture in a 20 mL screw cap vial, heat on a hot plate until the TATM solid dissolves, remove from the heat, and allow to cool to room temperature on its own, over the course of 1–2 h.

(C) Slow cooling: Seal same mixture in a 20 mL screw cap vial, dissolve the host on a hot plate, then place in a programmable temperature controlled oven, and allow to cool from 70 °C to room temperature at 1.2 °C per hour.

(D) Slow evaporation: Dissolve same mixture in a 20 mL vial at elevated temperature, allow to cool to room temperature while covered, then remove cap and allow excess guest to evaporate over the course of about 1 week.

(E) Stir 4 days at RT: Dissolve same mixture in a 20 mL vial, with a magnetic stir bar, and stir (covered) at room temperature for 4 days, then filter off excess solvent.

(F) Stir while cooling: Dissolve same mixture, stir on a stir plate (covered) as it cools to room temperature (~ 1 h), then filter.

The products were analyzed by a combination of techniques, including single crystal and powder X-ray diffraction (PXRD), and ¹³C CP/MAS NMR spectroscopy. Initially, if possible, several crystals from each batch were mounted on the single-crystal diffractometer and screened to obtain unit cell parameters and provide initial information on phase purity. The bulk products were identified both from the distinct multiplicities of the lines in the ¹³C solid NMR spectrum (arising from the differing contents of the respective asymmetric units), and from the presence of nonoverlapping reflections in the PXRD patterns. Once single-crystal structural data became available for the different forms, the PXRD patterns for the polycrystalline products obtained from the various preparative procedures were indexed. It should be noted that while single crystals of form 4 were obtained from the sides of the vial (near the initial solvent-vapor interface), the bulk product retained for NMR and PXRD analysis showed evidence of only a pure form 5 phase.

Single-crystal X-ray diffraction data were measured on a Bruker-Nonius Smart CCD diffractometer at either 125 or 173 K, using graphite monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) in the ω scan mode. The data reduction included a correction for Lorentz and polarization effects, with an applied empirical absorption correction. The crystal structures were solved by direct methods, and the structure was refined by full-matrix least-squares routines using the SHELXTL²⁴ program suite. Direct methods yielded all non-hydrogen host atoms and the partially occupied positions of Cl guest atoms. Initial positions for the partially occupied guest C atoms and the host hydrogen atoms were located from difference Fourier maps. The guest atom positions were initially refined with fixed isotropic thermal parameters and variable occupancy. As the refinement progressed, the guest C and Cl peaks were identified with distinct guest positions, group occupancies were refined, and the thermal parameter constraints were relaxed. Nearest neighbor and second neighbor distance constraints were imposed on the guest molecules. In the final stages of the refinement, guest hydrogens were placed in calculated positions and anisotropic thermal parameters were employed for those guest atoms of sufficient occupancy (greater than ~0.4 for C and 0.2 for Cl).

PXRD patterns were recorded at room temperature on a Rigaku Geigerflex vertical goniometer diffractometer using graphite monochromatized Co K_α radiation ($\lambda = 1.79$ Å) in the θ – θ scan mode. Samples were scanned over a range $10^\circ < 2\theta < 40^\circ$, with a 30 s accumulation time at an increment of 0.02° in 2θ , giving a total acquisition time for each sample of approximately 12 h.

The ¹³C CP/MAS NMR spectra were recorded at room temperature on a Bruker AMX 300 NMR spectrometer at a frequency of 75.483 MHz for ¹³C and 300.145 MHz for ¹H. The polycrystalline powder samples were spun in a 5 mm Doty magic-angle spinning (MAS) probe at frequencies between 5 and 6 kHz. The number of scans collected was approximately ten thousand, with 3.8 μ s 90° pulses, 5 ms cross polarization contact time, 51.2 ms acquisition time, and a 10 s recycle delay. Typically 4096 data points were accumulated with zero filling to 16 K, resulting in a digital resolution of about 2.4 Hz/point. The chemical shifts are given relative to tetramethylsilane at zero ppm, and were referenced externally (by rotor replacement) to the high field signal of hexamethylbenzene (16.9 ppm).

Results

(I) PXRD and ¹³C CP/MAS NMR:

The first and third forms (1 and 3) were prepared (as a mixture) by slow cooling (the details of the crystallization procedures are given in the experimental section). This preparation technique yielded single crystals, and after single-crystal X-ray diffraction experiments were completed, the crystals were ground up and subjected to additional experiments (e.g., PXRD and ¹³C CP/MAS NMR). The ¹³C CP/MAS NMR spectrum of the slow cooling product suggests that there are three host molecules in the asymmetric unit. This agrees with form 1 (3 host in A. U.), but not form 3 (2 host in A. U.). However, the experimental PXRD pattern contains components due to the calculated patterns from both forms 1 and 3. From the ¹³C solid NMR and our observations of the crystals, we have come to the conclusion that form 1 is the major component of the slow cooling sample, while form 3 is a minor component.

Pure form 2 was prepared separately by two different techniques, fast cooling and annealing at 50 °C. The sample used for single-crystal X-ray diffraction was made from the fast cooling procedure; however, when the crystals were ground up, both samples gave experimental PXRD patterns that could be matched to calculated patterns for form 2. By indexing the reflections of the experimental patterns, we were able to obtain the PXRD room temperature unit cell parameters of both samples, which were in good agreement with the single-crystal unit cell parameters of form 2.

Single crystals of forms 4 and 5 were prepared by slow evaporation. Form 4 is the minor component, while form 5 is the major component. We base this on the observation that we were able to fit the experimental PXRD pattern of the slow evaporation sample to the calculated pattern based on the crystal structure of form 5, but could not match it to the calculated pattern for form 4. In addition, we employed two more preparative techniques to yield polycrystalline samples of form 5, namely, stir while cooling and stir 4 days at room temperature. It should be noted that these last two preparative techniques yielded only polycrystalline powders. Both of these products displayed PXRD patterns that closely matched those calculated from form 5.

Table 1. Crystal Data, Data Collection and Final Refinement Parameters for the Five Crystal Forms of 1,3-Dichloropropane/TATM

	Crystal Data				
	1	2	3	4	5
form code	1	2	3	4	5
empirical formula	2 C ₁₉ H ₁₆ O ₃ S ₃ 1 C ₂ H ₄ Cl ₂	2 C ₁₉ H ₁₆ O ₃ S ₃ 1 C ₂ H ₄ Cl ₂	2 C ₁₉ H ₁₆ O ₃ S ₃ 1 C ₂ H ₄ Cl ₂	2 C ₁₉ H ₁₆ O ₃ S ₃ 1 C ₂ H ₄ Cl ₂	2 C ₁₉ H ₁₆ O ₃ S ₃ 1 C ₂ H ₄ Cl ₂
form wt (g/mol)	889.97	889.97	889.97	889.97	889.97
temperature (K)	125 (2)	173 (2)	173 (2)	173 (2)	173 (2)
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	P-1	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	C2/c
<i>a</i> (Å)	12.684(2)	14.319(3)	12.731(6)	12.715(3)	17.500(2)
<i>b</i> (Å)	12.704(4)	13.499(2)	12.762(6)	12.723(3)	18.465(3)
<i>c</i> (Å)	20.572(4)	22.328(2)	25.937(12)	13.893(3)	14.982(2)
α (°)	102.71(2)	90	90	90	90
β (°)	103.95(1)	104.081(2)	93.877(8)	109.967(4)	119.428(2)
γ (°)	91.35(2)	90	90	90	90
<i>V</i> (Å ³)	3128.1(12)	4186.3(7)	4204.4(3)	2112.5(8)	4216.6(10)
<i>Z</i>	3	4	4	2	4
<i>D</i> _{calc} (g/cm ³)	1.417	1.412	1.406	1.399	1.402
<i>F</i> (000)	1386	1848	1848	924	1848
μ (MoK α) (mm ⁻¹)	0.502	0.501	0.498	0.496	0.497
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
2 θ range (°)	1.05° < 2 θ < 29.59°	1.54° < 2 θ < 29.62°	1.57° < 2 θ < 25.68°	1.70° < 2 θ < 26.46°	1.73° < 2 θ < 29.69°
Data Collection					
crystal dimensions	0.25 × 0.30 × 0.40	0.20 × 0.20 × 0.35	0.08 × 0.35 × 0.45	0.15 × 0.15 × 0.23	0.15 × 0.20 × 0.30
index ranges	-17 ≤ <i>h</i> ≤ 17 -17 ≤ <i>k</i> ≤ 16 -28 ≤ <i>l</i> ≤ 28	-19 ≤ <i>h</i> ≤ 19 -18 ≤ <i>k</i> ≤ 18 -31 ≤ <i>l</i> ≤ 30	-15 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 15 -31 ≤ <i>l</i> ≤ 31	-15 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 15 -15 ≤ <i>l</i> ≤ 17	-24 ≤ <i>h</i> ≤ 24 -25 ≤ <i>k</i> ≤ 25 -19 ≤ <i>l</i> ≤ 20
reflections measured	39057	52066	39069	16361	26324
unique reflections	17221	11742	7971	4331	5965
<i>R</i> (int)	0.0269	0.0803	0.0769	0.0770	0.0492
Final Refinement: (full matrix least squares)					
Data/restraints/par	17221/21/876	11742/38/596	7971/14/586	4331/14/318	5965/14/318
GOF on <i>F</i> ²	1.011	0.918	1.028	0.932	1.012
final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0483 <i>wR</i> ₂ = 0.1351	<i>R</i> ₁ = 0.0559 <i>wR</i> ₂ = 0.1490	<i>R</i> ₁ = 0.0569 <i>wR</i> ₂ = 0.1503	<i>R</i> ₁ = 0.0522 <i>wR</i> ₂ = 0.1217	<i>R</i> ₁ = 0.0483 <i>wR</i> ₂ = 0.1251
highest peak (e Å ⁻³)	0.752	0.541	0.412	0.265	0.449
deepest hole (e Å ⁻³)	-0.868	-0.451	-0.585	-0.296	-0.310

(II) Single-crystal X-ray diffraction:

The crystal data, data collection, and refinement parameters for the five forms are summarized in Table 1. The *C*-centered cell of form **5** can be reduced to a primitive unit cell with *a* = 12.718 Å, *b* = 12.722 Å, *c* = 14.982 Å, α = 109.707°, β = 109.791°, γ = 93.074° (transformation matrix $\begin{smallmatrix} -1/2 & -1/2 & 0 \\ 0 & -1/2 & 1/2 \\ 0 & 0 & -1 \end{smallmatrix}$). Upon examination of all of the structural parameters, it becomes clear that forms **1**, **3**, **4**, and **5** all share a common planar motif characterized by *a* ~ *b* ~ 12.70 Å, with an included angle γ close to 90°. In all of these structures, the host TATM molecules are arranged in layers similar to those depicted in Figure 1 (form **1**). In general, one thienyl ring from each host molecule π -stacks with a thienyl ring from a neighboring host to form TATM dimers. The remaining two thienyl rings combine with those from a neighboring dimer (in the other direction) to form a cage or channel that encloses the included guest molecules, thus forming endless ribbons of TATM dimers that are aligned along a diagonal in the *a*+*b* or *a*-*b* directions. Adjacent ribbons are connected by weak aromatic C–H···O interactions. Subtle differences in the structural motifs are discussed below.

(a) Form **1**

Figure 1 depicts two packing diagrams of form **1**, which is triclinic, space group *P* $\bar{1}$. The principal axes of the unit cell are displayed in both diagrams, to show that the viewing perspective remains the same. Figure 1A shows a view down the *c** direction. The lattice is made up of endless ribbons running in the NW–SE

(110) direction. Channels, formed by the alignment of cages in adjacent layers, run perpendicular to the plane of the figure, parallel to the 111 direction. The 1,3-dichloropropane guests in the (*a b* 1/3) and (*a b* 2/3) layers (Figure 1A) are disordered over two inequivalent positions. Only the majority position (occupancy = 0.87) is depicted. Figure 1B depicts another view down the *c** direction; however, this view is of layers at (*a b* 0) and (*a b* 1). Note how the ribbons now run in a direction perpendicular to those in Figure 1A, namely, the NE–SW (110) direction. Within this layer, the guests lie across an inversion center and are disordered over two equivalent positions.

A unique feature of this structure is that the layer-repeat unit consists of three layers, rather than the more commonly encountered one or two layers. The repeat unit is composed of two layers with doubly disordered guest (DD) (Figure 1A), followed by one layer with symmetry disordered guest (SD) (Figure 1B). That is, the layers go as: SD–DD–DD–SD–DD–DD–SD... etc.

Finally, the host framework packing motif of form **1** is similar to that reported for *n*-hexane/TATM.^{4b} Both inclusion compounds crystallize in the triclinic *P* $\bar{1}$ space group, and the dimensions of the respective unit cells are almost identical, namely, *a*(Å) = 12.684 (12.647), *b*(Å) = 12.704 (12.694), *c*(Å) = 20.572 (20.604), and *V*(Å³) = 3128 (3173). However, the unit cell angles do not agree as those for form **1** are, by convention, all above 90°, while those for *n*-hexane/TATM are all below 90°, and a unit cell transformation, such as $\begin{pmatrix} \bar{1} & 0 & 0 & 0 & 1 & 0 & \bar{1} & 0 \end{pmatrix}$

Figure 1. Packing diagrams of form **1** of 1,3-dichloropropane/TATM obtained by single-crystal X-ray diffraction: (A) A view down the c^* direction. Ribbons in this figure run in the NW–SE (110) direction. The channels are parallel to $(-11-1)$. Only the majority position of the 1,3-dichloropropane guest is shown. (B) Another view down the c^* direction, however this view is of the layer adjacent to that in Figure 1A. Note how the ribbons now run in a direction perpendicular to those in Figure 1A, namely the NE–SW (1–10) direction. In addition, in this layer the guests are disordered over two equivalent positions.

Figure 2. Packing diagrams of form **2** of 1,3-dichloropropane/TATM obtained by single-crystal X-ray diffraction: (A) A view in the bc plane. The channel axis is perpendicular to the plane of the figure (the a direction). Notice how neighboring guests in the channel are markedly displaced from one another, giving rise to a pronounced zigzag type channel. Selected thienyl rings of the host are labeled. Refer to the text for details. (B) A view in the ab plane. The channel axis is in the plane of the figure and vertical in direction. Notice clearly that the guests are markedly displaced from one another as one traverses the channel.

$\bar{1}$), will make the comparison more reasonable. Finally, the contents of the asymmetric unit are slightly different for each. Form **1** contains three host molecules and 1.5 guest molecules, while the asymmetric unit of *n*-hexane/TATM contains three host molecules, but only one guest molecule. The *n*-hexane guests are located in channels between inequivalent guest layers.

(b) Form **2**

Figure 2 depicts two packing diagrams for form **2**. This structure is of the monoclinic $P2_1/n$ space group. The host lattice consists of pronounced zigzag channels in the a direction. From Figure 2B, a view in the ab plane, one sees that the chlorine atoms of the 1,3-

dichloropropane guests alternately point left and right as the channel is traversed in the a direction (the vertical direction in the figure). From this figure, one may also see that there are intermolecular close contacts (about the sum of VDW radii, 3.57 and 3.78 Å) between the chlorine atoms of neighboring guests within the host channel, which may serve to further stabilize the structure. The guest molecules are disordered over two inequivalent sites (occupancies 0.51:0.49).

The guest molecules from neighboring layers are displaced from one another, as depicted in Figure 2A, a view down the channel axis (a direction). We note, however, that Figure 2A may be misleading, as it

Figure 3. Packing diagrams of form **3** of 1,3-dichloropropane/TATM obtained by single-crystal X-ray diffraction: (A) A view showing one layer (ab plane). The ribbons run in the plane of the figure in the horizontal ($a+b$) direction. (B) Pairs of cages from adjacent layers overlap forming an extended cavity containing two guest molecules. A Cl–Cl approach distance of 4.12 Å is indicated (solid line).

appears that there is a large empty volume in the channel. However, when the guest's atoms are displayed as van der Waals radii (not shown), it is readily apparent that there is very little remaining free space in the host channel, despite neighboring guests being markedly displaced from one another. The observations above suggest that the “zigzag” of the channel in **2** is much more pronounced than that in the other forms. Indeed, as one can see in Figure 2A, there are four thienyl rings between guest sites (rather than the more commonly encountered two). From this figure (with labeled thienyl rings), two of the four thienyl rings (labeled as rings A and C in the figure) help to enclathrate the guest in the figure labeled as X, while the thienyl rings B and D (in an adjacent layer) help to enclathrate the guest labeled as Y. In one layer, thienyl ring B' helps to enclathrate guest X. In the adjacent layer, thienyl ring C' helps to enclathrate guest Y. In addition, the acetyl functionalities of thienyl rings A'' and D'' also participate in the formation of the channel

The cyclohexane **B**/TATM inclusion compound^{4f} (triclinic $P\bar{1}$) and others that are isostructural to it, such as TATM inclusions with benzene,^{4c} CCl_4 ,^{4d} cycloheptane,^{4f} and cyclooctane^{4f} bear some similarity to the present structure. These structures are all triclinic (space group $P\bar{1}$) and they have unit cell dimensions that can be related to those of form **2**. In particular they have $b \sim 13.7$ Å and $c \sim 14.2$ Å with an included angle (α) of $\sim 90^\circ$ (compares with b , a , and γ , respectively, of form **2**), while the a axis (~ 11.6 Å) is approximately half the c axis dimension of form **2** (~ 22.3 Å). The packing motifs are similar, with guests located in pronounced zigzag channels along the ~ 14.2 Å axes.

(c) Form **3**

Form **3** has an unusual bilayer motif. The asymmetric unit consists of two host molecules and one guest that is disordered (69:31) over two inequivalent positions (although one terminal Cl atom site is shared). As in most of the other forms, ribbons of TATM dimers are

aligned along the $a+b$ and $a-b$ directions. Figure 3A shows the layer at $(a,b,1/8)$. Inversion centers in the $(a,b,0)$ plane produce a second layer at $(a,b,-1/8)$. In the resulting bilayer, centered about $(a,b,0)$, the cages partially overlap, producing an extended cage (along c) that contains a pair of guest molecules (Figure 3B, closest Cl–Cl distance is 4.12 Å). The n glide produces a related bilayer centered about $(a,b,1/2)$, in which the ribbons run in the $a-b$ direction. To the best of our knowledge, this is the first reported TATM inclusion with this bilayer motif.

(d) Form **4**

Form **4** is similar to form **3**, but without the bilayer motif. The asymmetric unit consists of one TATM molecule and half a guest molecule. The guest molecule lies across an inversion center and is also disordered (58:42) over two inequivalent positions. The layer at $(a,b,0)$, Figure 4A, has ribbons (of cages and TATM dimers) aligned along the $a+b$ direction, while a c -glide produces a layer at $(a,b,1/2)$, as depicted in Figure 4B, with ribbons along $a-b$. The cages containing the guest molecules are isolated and do not form channels. This form is isostructural to the previously reported 1,2-dichloroethane/TATM monoclinic $P2_1/c$ structure.^{6a} The unit cell parameters for the 1,2-dichloroethane inclusion (and form **4**) are as follows: $a(\text{Å}) = 12.690$ (12.715), $b(\text{Å}) = 12.743$ (12.723), $c(\text{Å}) = 13.737$ (13.893), $\beta(^{\circ}) = 109.05$ (109.97), $V(\text{Å}^3) = 2100$ (2175). Both materials were determined to be minority components of their respective polymorphic mixtures, as estimated by ^{13}C CP/MAS NMR, to be about 1–10% abundant in our samples.

(e) Form **5**

We present two packing diagrams for form **5** of 1,3-dichloropropane/TATM in Figure 5. The first view, Figure 5A, is down the channel axis (c direction). The a axis is in the plane of the figure and horizontal in direction. From the figure, one sees that the lattice is made up of ribbons running in this direction. The ribbons are laid side by side to form layers in the ab

Figure 4. Packing diagrams of form 4 of 1,3-dichloropropane/TATM obtained by single-crystal X-ray diffraction: (A) A view down c (ab plane). Note how the ribbons run in the vertical ($a+b$) direction. (B) Another view in the ab plane, but of a layer adjacent to that in Figure 4A. Now the ribbons run in the horizontal ($a-b$) direction.

Figure 5. Packing diagrams of form 5 of 1,3-dichloropropane/TATM obtained by single-crystal X-ray diffraction: (A) A perspective view in the ab plane. The channels run in the c direction. (B) A view in the ac plane. Note the π -stacked thienyl rings running in the c (vertical) direction. The chlorine atoms of the guest alternately point toward and away from the viewer as the channel is traversed in the vertical (c) direction.

plane. In Figure 5A, it is also apparent that within each layer, each host cavity/guest molecule is surrounded in all four directions by a pair of π -stacked thienyl rings, while each pair of π -stacked thienyl rings is surrounded in all four directions by a host cavity/guest molecule. Again, two of the three thienyl rings of each host molecule participate in the formation of the channels. These channels contain guest molecules that lie across a 2-fold axis and are further disordered (68:32) over two inequivalent positions. The major difference between the layer motif observed in form 5 and those encountered for the similar forms 1, 3 and 4 is that the relatively large angle ($\beta \sim 119.43^\circ$) between the ribbon direction (a) and the c axis tilts the thienyl rings that form the channels so that they are directed toward the adjacent layer. The guest is located between layers within the channels formed by pairs of TATM molecules from adjacent layers. Also unique to form 5 is that the adjacent layers are arranged such that the cages overlap

and π -stacked thienyl rings overlap, forming infinite straight channels and infinite π -stacked columns along c , respectively. Figure 5B, a view in the ac plane, shows these channels and infinite π -stacked columns. The other conclusion that may be reached from this figure is that the channels are of a slight zigzag type. This is in contrast to form 2 (see above), for which the zigzag of the channel is much more pronounced. In the present structure, as the channels are traversed in the vertical (c) direction, the chlorine atoms of the guest alternately point toward and away from the viewer (see Figure 5B). The guest molecule's long axis extends approximately along the channel axis with Cl–Cl distances between neighboring guests of 3.65–3.82 Å. Form 5 is isostructural to an unpublished structure of 1,3-dibromopropane/TATM.²⁵ They both crystallize in the monoclinic $C2/c$ space group, and the unit cell parameters for 1,3-dibromopropane/TATM (and form 5 of 1,3-dichloropropane/TATM) are as follows: $a(\text{\AA}) = 17.581(17.500)$; $b(\text{\AA})$

Table 2. Torsion Angles for TATM Host Molecules of the Present Study

form	fragment	torsion angle (°)	orientation of C=O wrto S
1	H1–C1–C2–C3	–1.2	<i>S</i>
	H1–C1–C8–C9	103.7	<i>S</i>
	H1–C1–C14–C15	154.8	<i>S</i>
	H1'–C1'–C2'–C3'	–6.2	<i>S</i>
	H1'–C1'–C8'–C9'	100.9	<i>S</i>
	H1'–C1'–C14'–C15'	159.3	<i>S</i>
	H1*–C1*–C2*–C3*	1.1	<i>S</i>
	H1*–C1*–C8*–C9*	100.5	<i>S</i>
	H1*–C1*–C14*–C15*	154.8	<i>S</i>
2	H1–C1–C2–C3	–11.9	<i>S</i>
	H1–C1–C8–C9	131.0	<i>S</i>
	H1–C1–C14–C15	145.0	<i>A</i>
	H1'–C1'–C2'–C3'	–11.4	<i>S</i>
	H1'–C1'–C8'–C9'	130.7	<i>S</i>
	H1'–C1'–C14'–C15'	148.0	<i>A</i>
3	H1–C1–C2–C3	–2.7	<i>S</i>
	H1–C1–C8–C9	101.4	<i>S</i>
	H1–C1–C14–C15	161.0	<i>S</i>
	H1'–C1'–C2'–C3'	–0.2	<i>S</i>
	H1'–C1'–C8'–C9'	101.7	<i>S</i>
	H1'–C1'–C14'–C15'	156.7	<i>S</i>
4	H1–C1–C2–C3	–0.9	<i>S</i>
	H1–C1–C8–C9	102.2	<i>S</i>
	H1–C1–C14–C15	154.9	<i>S</i>
5	H1–C1–C2–C3	7.1	<i>S</i>
	H1–C1–C8–C9	106.8	<i>S</i>
	H1–C1–C14–C15	154.4	<i>S</i>

= 18.401 (18.465); $c(\text{\AA}) = 15.008$ (14.982); $\beta(^{\circ}) = 119.35$ (119.43); $V(\text{\AA}^3) = 4232$ (4217).

Discussion

Table 2 summarizes the torsion angles for the nine crystallographically independent TATM molecules from the five crystal structures of the present work. The TATM molecules are individually chiral; however, all of the presently reported structures are centrosymmetric. As there was no attempt to ensure that the asymmetric unit contained TATM molecules of the same "chirality", in tabulating the data it was necessary to check the torsion angles of both the TATM molecules in the asymmetric unit and those related through an inversion center. The atomic numbering scheme and torsion angle ordering are as discussed by Herbstein.⁸ In Table 2, one may notice that for forms **1**, **3**, **4**, and **5**, the conformations of each the three thienyl rings about the central methine C–H bond are each very similar. For these four forms, the thienyl ring that is approximately coplanar to the C–H bond has torsion angles ranging from –6.2° to 7.1°, the next largest torsion angle varies from 100.50° to 106.78°, while the largest angle varies from 154.4° to 161.0°. Furthermore, all four of these structures suggest that the universal orientation of the carbonyl bond of the acetyl groups is toward the direction of the sulfur atom of its associated thienyl ring (i.e., all 7 structures are *SSS*, where *S* means syn).

On the other hand, form **2** displays unique torsion angles as compared to the other four structures of the present study. Furthermore, both of the crystallographically unique TATM molecules of form **2** have torsion angles that are again very similar to each other, and both indicate that one of the three carbonyl groups of each host points away from its associated thienyl ring sulfur (*SSA* – where *A* means anti). This behavior is

Table 3. Torsion Angles for TATM Host Molecules as Reported in the Literature⁸

guest	host molecule	$\tau_1(^{\circ})$	$\tau_2(^{\circ})$	$\tau_3(^{\circ})$	orientation of C=O (wrto S)
ethyl acetate	A	7.0	102.9	157.0	<i>SSS</i>
	A	–3.2	110.7	160.0	<i>SSS</i>
	A	–12.6	109.4	162.8	<i>SSS</i>
	A	2.4	108.2	156.8	<i>SSS</i>
	A	0.6	110.1	157.6	<i>SSS</i>
benzene	A	–16.2	126.2	148.2	<i>SSA</i>
	B	–10.1	124.2	148.7	<i>SSA</i>
	A	–20.0	129.0	148.3	<i>SSA</i>
cyclohexane	A	–11.1	129.5	151.0	<i>SSA</i>
	B	–18.7	128.6	149.4	<i>SSA</i>
cycloheptane	A	–12.2	130.4	150.2	<i>SSA</i>
	B	–17.1	129.6	148.0	<i>SSA</i>
cyclooctane	A	16.6	130.1	146.5	<i>SSA</i>
	B	–13.9	132.2	151.9	<i>SSA</i>
cyclononanone	A	–7.3	101.8	–15.2	<i>SSS</i>

not surprising, because form **2** does not exhibit the same layer structure.

Next, it is interesting to compare our torsion angles with those reported in 1997 by Herbstein.⁸ On the basis of the crystal structures of TATM inclusion compounds that were available at the time,^{3,4} he classified the structures according to the torsional angles of the thienyl rings about the central methine C–H bond of the host: the data indicated that there were only three general types of host torsional conformation (see Table 3). They were as follows: (conformation #1) $\tau_1 \sim 0^{\circ}$, $\tau_2 \sim 105^{\circ}$, $\tau_3 \sim 160^{\circ}$, *SSS*; (conformation #2) $\tau_1 \sim 0^{\circ}$, $\tau_2 \sim 130^{\circ}$, $\tau_3 \sim 150^{\circ}$, *SSA* and (conformation #3) $\tau_1 \sim 0^{\circ}$, $\tau_2 \sim 100^{\circ}$, $\tau_3 \sim -15^{\circ}$, *SSS*. In the present study, we see similar results. Forms **1**, **3**, **4**, and **5** have torsional angles that are similar to those of Herbstein's conformation #1, while form **2** possesses torsions that are similar to Herbstein's conformation #2. Herbstein noted that the range of torsion angles within each of the three conformational groups did not exceed 10°; in our case the largest variation is 13.3° (for the smallest torsion angle). The range for the other two torsion angles are both less than 10°. Finally, conformation #3 was found by Herbstein to occur only for the cyclononanone/TATM inclusion compound.^{4e} A recently reported water/TATM inclusion^{6b} also displays similar torsion angles (–3.5°, 99.6°, –23.8°, *SSS*) and may have similar structural features.

In Herbstein's work, he found approximately equal occurrences of *SSA* (10) and *SSS* (7). In the present study, we found only two occurrences of *SSA*, while seven TATM molecules have an *SSS* conformation. Herbstein also suggested that when there is more than one TATM molecule in the asymmetric unit (for guests benzene,^{4c} carbon tetrachloride,^{4d} cyclohexane **B**,^{4f} cycloheptane,^{4f} cyclooctane^{4f} and *n*-hexane^{4b}), the two or three host molecules (within each structure) have approximately the same conformation. We found the same behavior in the present study. For the 1,3-dichloropropane/TATM structures that have more than one host molecule in the asymmetric unit (forms **1**, **2** and **3**), one observes nearly identical TATM torsion angles within each form. Finally, as reported by Herbstein, within each of the five types of TATM structures

(based on the crystallographic unit cell parameters), the same TATM conformation is observed in each group.

As a further illustration of this, form **1** has similar unit cell parameters to *n*-hexane/TATM,^{4b} and both belong to Herbstein's conformation group #1. Although they have different unit cell parameters, form **2** has a packing motif that is very similar to both cyclohexane **B**/TATM^{4f} and carbon tetrachloride/TATM.^{4d} All three inclusion compounds belong to Herbstein's conformational group #2. Form **4** of the present study is isostructural to 1,2-dichloroethane **B**/TATM,^{6a} and as expected, both have very similar torsional angles ($\tau_1 \sim 1.3^\circ$, $\tau_2 \sim 105.3^\circ$, $\tau_3 \sim 156.2^\circ$, SSS for the latter structure). Finally, form **5** is isostructural to the unpublished structure of the 1,3-dibromopropane/TATM inclusion compound.²⁵ Both also have nearly identical host torsions, those for the latter structure are as follows: $\tau_1 \sim 8.2^\circ$, $\tau_2 \sim 105.3^\circ$, $\tau_3 \sim 153.7^\circ$, SSS. These observations lend further support to Herbstein's conclusion that TATM inclusion compounds with similar unit cell parameters (or similar packing motifs) will display similar torsional angles for the TATM host molecules.

The other manner in which one can correlate the torsion results is to see if each TATM polymorph (identical guests that crystallize in more than one form) have similar torsions and unit cell parameters. There are three TATM polymorphs reported so far, namely, cyclohexane^{4f} (2 forms), 1,2-dichloroethane^{6a} (2 forms), and 1,3-dichloropropane (5 forms). For cyclohexane, each of the two forms have both different unit cell parameters and TATM torsions. For 1,2-dichloroethane, the two forms have different unit cell parameters but very similar host torsional angles. In this case, the triclinic cell in the *standard setting* does not appear at first glance to contain an *ab* layer similar to that observed in the monoclinic form. However, the ($\bar{1}$ 1 1) reciprocal lattice plane of the triclinic form is indeed similar to the *ab* plane of the monoclinic form. For the guest of the present study, each of the five forms have unique unit cell parameters, while four of the five forms have very similar host torsion angles. These four forms (**1**, **3**, **4**, and **5**) have very similar dimensions of the *ab* plane, as discussed above.

As far as the conformation of the 1,3-dichloropropane guests are concerned (as depicted in Table 4) four of the five forms (**1**, **3**, **4**, and **5**) have one guest as *gauche-gauche* and a second guest as *gauche-trans*. For these four structures, the conformational torsions of the host are all very similar (see above). On the other hand, the polymorph with a unique host conformation (form **2**) also has a unique guest conformation, namely, both guests as *gauche-trans*. So we see an interesting relationship between the host conformation and the guest conformation of these inclusion compounds. Gas phase²⁶ and liquid phase²⁷ studies of pure 1,3-dichloropropane have concluded that the *gauche-gauche* (major) and *gauche-trans* (minor) conformations are predominant. In the solid state, 1,3-dichloropropane exists solely in the *gauche-gauche* conformation.²⁸

To date, it has only been possible to produce pure bulk samples of form **2** and form **5**. The remaining forms have been produced only as mixtures. The morphology of all of the crystal forms appears to be similar. Crystals examined under the microscope all appeared to be

Table 4. Torsion Angles for 1,3-Dichloropropane Guest Molecules of the Present Study

form	fragment	torsion angle (°)	conformation	occupancy
1	CL1–C101–C102–C103	56.5	G	0.87
	C101–C102–C103–CL2	57.4	G	
	CL3–C104–C105–C106	105.3	intermediate	0.13
2	C104–C105–C106–CL4	58.4	G	
	CL5–C201–C202–C203	–69.5	G	0.50
	C201–C202–C203–CL6	179.3	T	
	CL2A–C02–C01–C03	41.4	G	0.49
	C02–C01–C03–CL3A	–174.5	T	
	CL2B–C05–C04–C06	–176.5	T	0.51
3	C05–C04–C06–CL3B	65.5	G	
	C1A–C101–C102–C103	64.2	G	0.69
	C101–C102–C103–CL2A	52.1	G	
	CL1B–C201–C202–C203	55.8	G	0.31
4	C201–C202–C203–CL2B	–165.5	T	
	CL01–C001–C002–C003	–75.8	G	0.57
	C001–C002–C003–CL02	–164.0	T	
	CL03–C004–C005–C006	77.8	G	0.43
5	C004–C005–C006–CL04	–47.5	G	
	CL01–C01–C02–C03	59.4	G	0.68
	C01–C02–C03–CL02	62.8	G	
	CL03–C04–C05–C06	–58.6	G	0.32
	C04–C05–C06–CL04	168.0	T	

rectangular plates or blocks. The color of the crystals was pale yellow/light orange, similar to that reported for most other TATM inclusions. The calculated densities of all five forms show little variation (see Table 1).

In the context of inclusion compounds, extensive polymorphism might be expected, as the existence of several energetically similar forms is an intrinsic feature of supramolecular materials based on weak interactions.²⁹ Surprisingly, very little is known about polymorphism of inclusion compounds if one excludes pseudopolymorphism, for which the composition is not constant. Only two examples have been reported: dimorphs are known for both gossypol³⁰ and the title host.^{4f,6a} However, it may be another case of the more one looks, the more one will find.

Conclusions

This paper presents structural work on five polymorphic modifications of TATM/1,3-dichloropropane, reporting detailed variations in crystal packing and the torsional conformations of both host and guest molecules. These are discussed and compared with earlier results on TATM inclusions as reported by Herbstein.⁸ From our results, one may predict that the possibility of producing conformational isomers of both host and guest molecules may well provide a road map for preparing a large number of polymorphs, thus giving unparalleled opportunities for the study of this complex phenomenon.

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Supporting Information Available: Tables of reduced atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for each of the five reported crystal structures along with crystallographic information files. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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