Structural Rationalisation of Co-crystals Formed between Trithiocyanuric Acid and Molecules Containing Hydrogen Bonding Functionality

Shinbyoung Ahn,[a] J. PrakashaReddy,[b] Benson M. Kariuki,[a] Swati Chatterjee,[c] Anupama Ranganathan,[c] V. R. Pedireddi,*[b] C. N. R. Rao,*[c] and Kenneth D. M. Harris*[d]

Abstract: Crystallisation of trithiocyanuric acid (**TTCA**) from various organic solvents that have hydrogen bonding capability (acetone, 2-butanone, dimethylformamide, dimethyl sulfoxide, methanol and acetonitrile) leads to the formation of co-crystals in which the solvent molecules are incorporated together with **TTCA** in the crystal structure. Structure determination by single-crystal X-ray diffraction reveals that these co-crystals can be classified into different groups depending upon the topological arrangement of the **TTCA** molecules in the crystal structure. Thus, three different types of single-tape arrangements of **TTCA** molecules and one type of double-tape arrangement of **TTCA** molecules are identified. In all co-crystals, hydrogen-bonding interactions are formed through the involvement of N–H bonds of **TTCA** molecules in these tapes and the other molecule in the co-crystal. Detailed rationalisation of the structural properties of these co-crystals is presented.

Keywords: crystal engineering · hydrogen bonds · nitrogen heterocycles · structure elucidation

Introduction

There is currently considerable interest in the design and preparation of crystalline molecular solids with specific targeted structures. Within this field of “crystal engineering”,[1] the aim is often to target a structure that will give rise to a specific desired solid-state property, such as chemical reactivity, electrical, optical or magnetic properties. In this regard, the study of hydrogen-bonded materials[2] has been widely exploited, based on the fact that the hydrogen bond is generally stronger and more directional than the other types of intermolecular force that are typically present in organic molecular crystals; as a consequence, rationalisation and/or prediction of the structural properties of such materials can often be achieved straightforwardly on the basis of understanding the preferential formation of specific types of hydrogen-bonded array. In many cases in which the desired material contains two or more molecular components (i.e. co-crystals), the target structures can be prepared by co-crystallisation of the constituent molecules from a suitable solvent. Solvent interference in such co-crystallisation processes is often negligible, although in some cases the solvent can play a critical role in directing the crystallisation process towards a particular crystal structure. As an illustration,[3] a complex of 3,5-dinitrobenzoic acid and anthracene is formed only when crystallisation is carried out in the presence of benzene—the benzene molecules join adjacent dimers of 3,5-dinitrobenzoic acid through C–H···O hydrogen bonds to yield a hexagonal architecture with cavities that are filled by the anthracene molecules. In other cases, different solvents can actively direct the formation of different types of crystal structures (i.e. polymorphs[4]), without actually being incorporated into the crystal structure. Examples include the formation[5] of different polymorphic forms of *trans*-cinnamic acid and several of its derivatives by crystallisation from dif-

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[a] Dr. S. Ahn, Dr. B. M. Kariuki
School of Chemistry, University of Birmingham
Edgbaston, Birmingham B15 2TT (UK)

[b] J. PrakashaReddy, Dr. V. R. Pedireddi
Division of Organic Chemistry, National Chemical Laboratory
Pune 411 008 (India)
E-mail: pediredi@ems.ncl.res.in

[c] Dr. S. Chatterjee, Dr. A. Ranganathan, Prof. C. N. R. Rao
Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064 (India)
E-mail: cnrrao@jncasr.ac.in

[d] Prof. K. D. M. Harris
School of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, Wales (UK)
Fax: (+44) 292-087-4030
E-mail: harriskdm@cardiff.ac.uk

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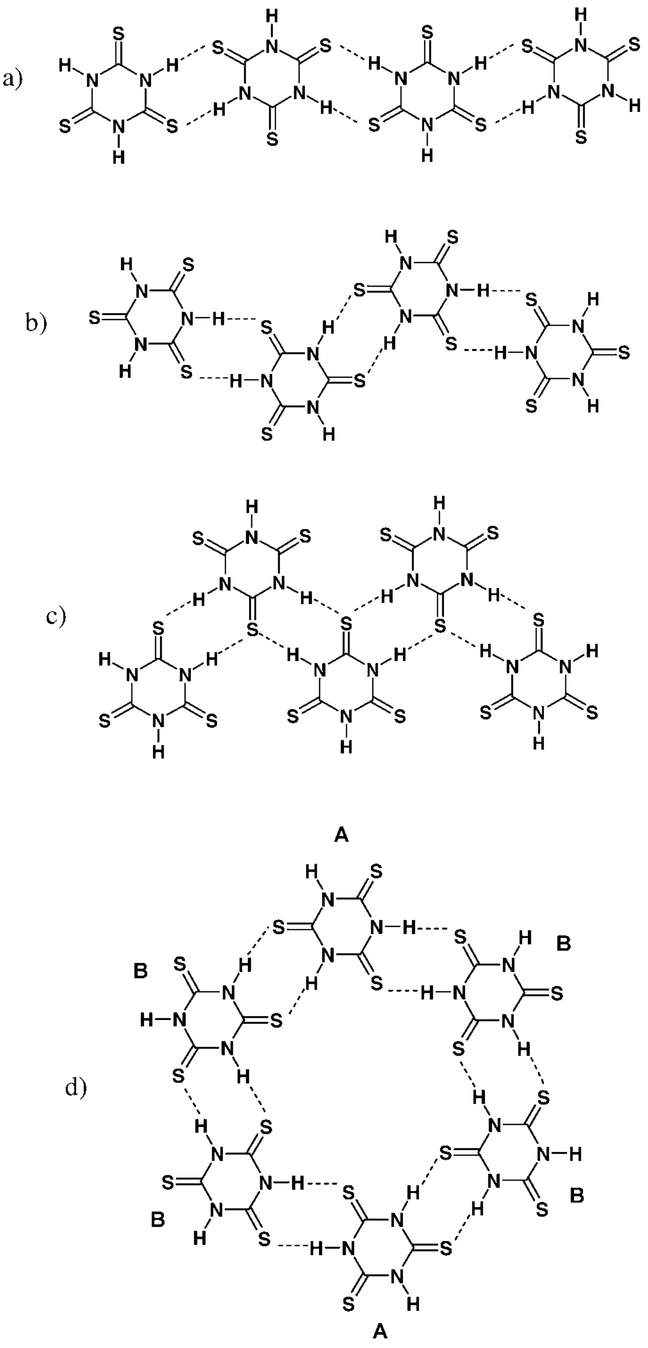
ferent solvents, the isolation and characterisation[6] of three polymorphic forms of 2-amino-5-nitropyrimidine during attempts to co-crystallise this molecule with 2-amino-5-nitropyridine, and the formation[7] of two polymorphic forms of thiodiglycolamide during attempts to co-crystallise this molecule with 4,4′-bipyridyl.

Among the wide range of molecular co-crystals that have been studied within the context of crystal engineering design strategies, there have been several studies[8] of co-crystals containing cyanuric acid as one of the components, based upon exploitation of the fact that this molecule should form hydrogen bonded arrays with well-defined and predictable structural properties (at least in two-dimensions). To date, substantially less attention[9] has been devoted to studies of the sulfur analogue of cyanuric acid—trithiocyanuric acid (**TTCA**). Nevertheless, rationalisation of the structure of the co-crystal formed between **TTCA** and acetone,[9a] suggests that it might be possible to prepare other co-crystals of TTCA by crystallisation of this molecule from solvents that are capable of forming hydrogen bonds with **TTCA**. With this motivation, we have found that crystallisation of **TTCA** from a variety of different hydrogen-bonding solvents (acetone, 2-butanone, dimethylformamide, dimethyl sulfoxide, methanol and acetonitrile) leads to a range of solvate crystal structures. In this paper, we present a rationalisation of structural features in co-crystals formed between **TTCA** and molecules that possess hydrogen bonding functionality, with the expectation that many of these features may be generally applicable in the design and rationalisation of a wider range of co-crystal structures than those studied in the present work.

Results and Discussion

Identification of characteristic packing modes for TTCA molecules

Structural rationalisation of the materials studied in this work reveals two structural classes—infinite single-tape structures (Scheme 1a–c) and infinite double-tape structures (Scheme 1d). For the single-tape structures, there are three different types of tape, labelled types 1, 2 and 3 (Scheme 1a, b and c respectively).



Scheme 1.

First, we highlight features of the different types of single-tape structure. In all three types of single-tape, each **TTCA** molecule interacts with two neighbours. Each of these interactions involves a pair of N−H···S hydrogen bonds in a cyclic $R^2_2(8)$ arrangement. In tapes of types 1 and 2, these interactions involve two N−H bonds and two C=S bonds of the **TTCA** molecule, and thus one N−H bond and one C=S bond in each molecule are not involved in these interactions (these "free" groups are thus available to participate in hydrogen bonds external to the tape). In type 1, the "free" N−H bond and C=S bond are at opposite corners of the molecule, whereas in type 2, the "free" N−H bond and C=S bond are at adjacent corners of the molecule. In type 3, the $R^2_2(8)$ hydrogen-bonding arrangement between adjacent molecules involves two N−H bonds but only one C=S bond of each **TTCA** molecule, and thus one N−H bond and two C=S bonds of each molecule are not involved in these interactions. Thus, in all types of single-tape, there is one "free" N−H bond per molecule. The significance of this fact is discussed later. In all types of single-tape, the direction of the "free" N−H bond alternates between opposite sides of the tape on moving from one molecule to its neighbour along the tape. In tapes of types 1 and 3, the "free" N−H bond points perpendicular to the direction of the tape, whereas in tapes of type 2, the "free" N–H bond forms an angle of about 60° with the direction of the tape. In all types of single-tape, the periodic repeat unit of the tape comprises two **TTCA** molecules, but because the packing of **TTCA** molecules is different in each case, the periodic repeat distance along the direction of the tape is different for each type of tape (in Scheme 1a–c, the periodicity can be viewed in terms of the periodicity of "free" N–H bonds). Thus, the periodic repeat distance is about 12.8 Å for tapes of type 1, about 11.3 Å for tapes of type 2 and about 8.8 Å for tapes of type 3. Corresponding to the trend of decreasing periodicity from type 1 to type 3, the width of the tapes becomes greater on moving from type 1 to type 3.

The double-tape structure consists of two single-tapes of type 2 that are cross-linked to each other through pairs of N–H···S hydrogen bonds in cyclic $R_2^2(8)$ arrangements. Within each of the individual single-tapes, every second molecule is linked to a molecule of the other single-tape by such cross-linking interactions. For the molecules (denoted type B molecules) involved in cross-linking between the two individual single-tapes, all N–H bonds and all C=S bonds are engaged in N–H···S hydrogen bonds to other **TTCA** molecules. The other molecules (denoted type A molecules), on the other hand, have the same hydrogen bonding topology as the molecules in the type 2 single-tape discussed above, and therefore have one "free" N–H bond and one "free" C=S bonds that are not involved in hydrogen bonding to other **TTCA** molecules. These "free" N–H and C=S bonds are at adjacent corners of the **TTCA** molecule and point outwards from the double-tape (the "free" N–H bond forms an angle of about 60° with the direction of the double-tape). Clearly half of the **TTCA** molecules in the double-tape are of type A and the other half are of type B. Within the double-tape, groups of six **TTCA** molecules forming a cyclic hydrogen-bonded arrangement (involving two cross-links) may be identified; the region at the centre of this cyclic arrangement represents a "van der Waals hole" within the double-tape.

Discussion of specific structures

Structures of TTCA/acetone and TTCA/2-butanone: The co-crystals **TTCA**/acetone (structure reported previously[9a]) and **TTCA**/2-butanone both have a 2:1 ratio of **TTCA** to acetone or 2-butanone, and both structures adopt essentially the same packing arrangement (Figure 1a,b). The **TTCA** molecules are arranged in the double-tape structure, and each "free" N–H bond on the **TTCA** double-tape forms an N–H···O=C hydrogen bond to the oxygen atom of an acetone or 2-butanone molecule. All **TTCA** molecules of type A are linked to an acetone or 2-butanone molecule in this way, corresponding to the 2:1 molar ratio discussed above. On either side of a given tape, there are two other tapes in the same plane, with the directions of these tapes running parallel to each other. The pendant acetone or 2-butanone molecules of adjacent tapes alternate with one another, and in the region between adjacent tapes, the repeat unit along the direction of the tape comprises a pendant acetone or 2-butanone molecule from one tape, a pendant acetone or 2-butanone molecule from the other tape, and the sulfur atoms of a "free" C=S bond from each tape (S···S distance 4.31 Å for **TTCA**/acetone and 5.13 Å for **TTCA**/2-butan-

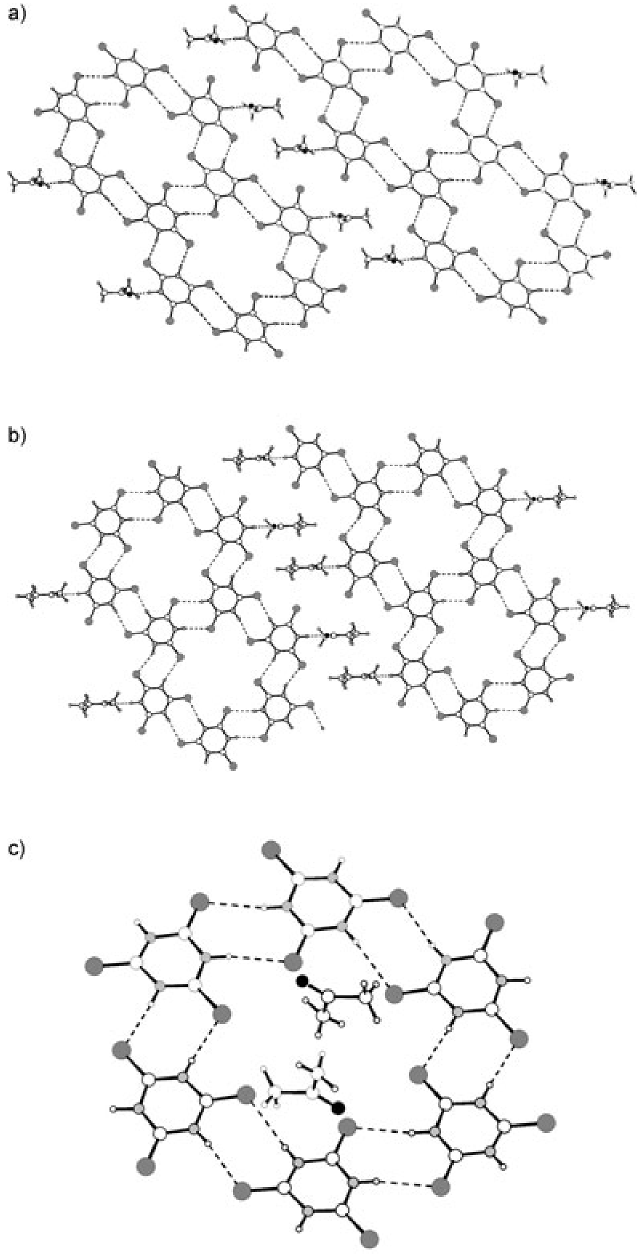


Figure 1. a) A single sheet in the crystal structure of the **TTCA**/acetone co-crystal, viewed perpendicular to the sheet, showing the double-tapes of **TTCA** molecules. Dashed lines indicate hydrogen bonding interactions. b) A single sheet in the crystal structure of the **TTCA**/2-butanone co-crystal, viewed perpendicular to the sheet, showing the double-tapes of **TTCA** molecules. Dashed lines indicate hydrogen bonding interactions. c) Figure showing the methyl groups of acetone molecules in the **TTCA**/acetone co-crystal pointing towards the "van der Waals hole" in an adjacent sheet. The acetone molecule at the upper right lies in the sheet above the one shown, and the other acetone molecule lies in the sheet below the one shown.

one). In both structures, the plane of the acetone or 2-butanone molecule (defined by the plane of the $O{=}C(C)_2$ unit) is approximately perpendicular to the plane of the **TTCA** tape. In the **TTCA**/acetone structure, one $C{-}CH_3$ bond lies approximately in the plane of the **TTCA** tape, and the other $C{-}CH_3$ bond projects outwards from this plane. In the **TTCA**/2-butanone structure, the $C{-}CH_2CH_3$ bond lies approximately in the plane of the **TTCA** tape, and the $C{-}CH_3$ bond projects outwards from this plane.

We now discuss the relative packing of the two-dimensional sheets discussed above. In both structures, adjacent sheets are displaced parallel to the plane of the sheets, and the perpendicular distance between adjacent sheets is about 3.5 Å for **TTCA**/acetone and about 3.6 Å for **TTCA**/2-butanone. In both cases, the relative positions of the **TTCA** molecules in adjacent sheets is such that S atoms of one sheet lie almost directly above N atoms of the adjacent sheet, and *vice versa*. Importantly, the relative displacement of adjacent sheets is such that the $C{-}CH_3$ bonds of the acetone or 2-butanone molecules that project out of the plane of a given sheet (see above) point towards the centre of the cyclic arrangements within the **TTCA** double-tape of an adjacent sheet, such that the methyl group effectively nestles into the "van der Waals hole" at the centre of the cyclic arrangement (Figure 1c). This feature allows adjacent sheets to pack together efficiently, and may indeed be one factor responsible for the formation of double-tapes of **TTCA** molecules in these structures. We note that the single-tapes of **TTCA** molecules do not contain "van der Waals holes" of this type. Furthermore, the molecules (dimethyl sulfoxide, dimethylformamide and acetonitrile; see below) that form sheet-like structures containing single-tape arrangements of **TTCA** molecules do not have groups that project out from the plane of the sheets (such as the methyl groups in the **TTCA**/acetone and **TTCA**/2-butanone structures).

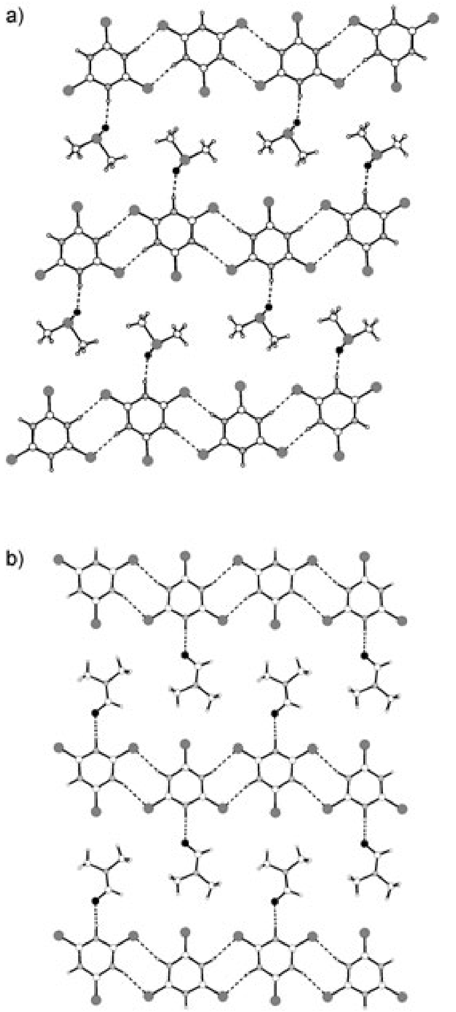


Figure 2. a) A single sheet in the crystal structure of the **TTCA**/dimethyl sulfoxide co-crystal, viewed perpendicular to the sheet, showing the single-tapes of **TTCA** molecules of type 1. Dashed lines indicate hydrogen bonding interactions. b) A single sheet in the crystal structure of the **TTCA**/dimethylformamide co-crystal, viewed perpendicular to the sheet, showing the single-tapes of **TTCA** molecules of type 1. Dashed lines indicate hydrogen bonding interactions.

Structures of TTCA/dimethyl sulfoxide and TTCA/dimethylformamide: The co-crystals **TTCA**/dimethyl sulfoxide and **TTCA**/dimethylformamide each have a 1:1 ratio of the two components. Although the crystal symmetry of these structures is different, the basic two-dimensional packing arrangements are very similar (Figure 2), and both structures comprise single-tapes of **TTCA** molecules of type 1. The "free" N−H bond of each **TTCA** molecule in the tape forms an N−H···O hydrogen bond to the oxygen atom of a dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) molecule. On each side of a given tape there is another tape in the same plane, giving rise to a two-dimensional sheet. Within this plane, all tapes run parallel to each other. In the region between adjacent tapes, the pendant DMF or DMSO molecules of adjacent tapes alternate with one another and interact through van der Waals interactions (in contrast, in the co-crystals of cyanuric acid with DMSO and DMF, these molecules exist as dimer pairs linked to each other by C−H···O interactions). In the **TTCA**/DMF structure, the non-hydrogen atoms of the DMF molecule lie in the plane of the **TTCA** tape, and in the **TTCA**/DMSO structure, the non-hydrogen atoms of the DMSO molecule lie approximately in this plane (recalling that the DMSO molecule is itself non-planar).

The two-dimensional sheets discussed above are stacked parallel to each other; the perpendicular distance between adjacent sheets is about 3.4 Å for **TTCA**/DMF and about 3.6 Å for **TTCA**/DMSO. In the **TTCA**/DMSO structure, the relative positions of the **TTCA** molecules in adjacent sheets are such that S atoms of one sheet lie almost directly above N atoms of the adjacent sheet, and *vice versa*. In the **TTCA**/DMF structure, on the other hand, each **TTCA** molecule has an S atom of a **TTCA** molecule in one adjacent sheet lying almost directly above the centre of its ring.

Structure of TTCA/acetonitrile: The co-crystal of **TTCA**/acetonitrile has a 1:1 ratio of the two components, and com-

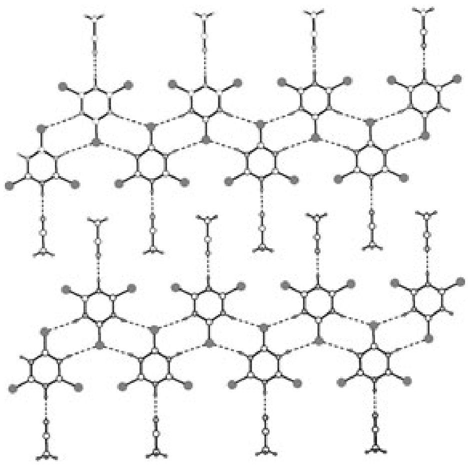


Figure 3. A single sheet in the crystal structure of the **TTCA**/acetonitrile co-crystal, viewed perpendicular to the sheet, showing the single-tapes of **TTCA** molecules of type 3. Dashed lines indicate hydrogen bonding interactions.

prises single-tapes of **TTCA** molecules of type 3 (Figure 3). The "free" N–H bond of each **TTCA** molecule forms an N–H···N hydrogen bond to the nitrogen atom of the acetonitrile molecule. On each side of a given tape there is another tape in the same plane, giving rise to a two-dimensional sheet. The pendant acetonitrile molecules of adjacent tapes alternate with one another in the region between the tapes. The relative packing of the two-dimensional sheets reflects many of the features discussed above for other co-crystals of **TTCA**. Thus, the relative positions of the **TTCA** molecules in adjacent sheets is such that S atoms of one sheet lie almost directly above N atoms of the adjacent sheet, and vice versa. The perpendicular distance between adjacent sheets is about 3.4 Å.

It is interesting to speculate on the formation of single-tapes of type 1 for the **TTCA**/DMSO and **TTCA**/DMF co-crystals and single-tapes of type 3 for the **TTCA**/acetonitrile co-crystal. As discussed above, the periodicity along the direction of the tape (and hence the periodicity of "free" N–H bonds) is larger for a single-tape of type 1 than a single-tape of type 3. Thus, for hydrogen bond acceptor molecules (such as DMSO and DMF) that are sufficiently bulky, it may be impossible to accommodate these molecules pendant to a tape of type 3 due to the close spacing of hydrogen bond donor N–H bonds along the periphery of the tape. However, a less bulky molecule (such as acetonitrile) can be accommodated pendant to this type of tape. For single-tapes of type 1, on the other hand, the greater spacing of N–H bonds along the direction of the tape is sufficient to accommodate the bulkier DMSO and DMF molecules pendant to the tape.

Structure of TTCA/methanol: For all of the co-crystals discussed above, the "other" molecule (acetone, 2-butanone, DMSO, DMF and acetonitrile) contains a good hydrogen bond acceptor but does not contain a good hydrogen bond donor. It is not surprising that, in all of these structures, each of these molecules engages as a hydrogen bond acceptor in a hydrogen bond with a "free" N–H bond of a **TTCA** molecule. The co-crystal formed between **TTCA** and methanol presents additional possibilities, as methanol can behave both as a hydrogen bond donor and as a hydrogen bond acceptor.

The co-crystal of **TTCA** and methanol has a 1:1 ratio of the two components. In this structure (Figure 4), the **TTCA** molecules are arranged in single-tapes of type 2 (Figure 4a), and the "free" N–H bond of each **TTCA** molecule forms an N–H···O hydrogen bond to the oxygen atom of a methanol molecule. The methyl group of the methanol molecule lies approximately in the plane of the tape. While the existence of a **TTCA** tape with pendant "solvent" molecules hydrogen bonded through the "free" N–H bonds on the tape is a common feature of all the co-crystal structures reported in this paper, the arrangement of tapes relative to each other differs significantly between the **TTCA**/methanol co-crystal

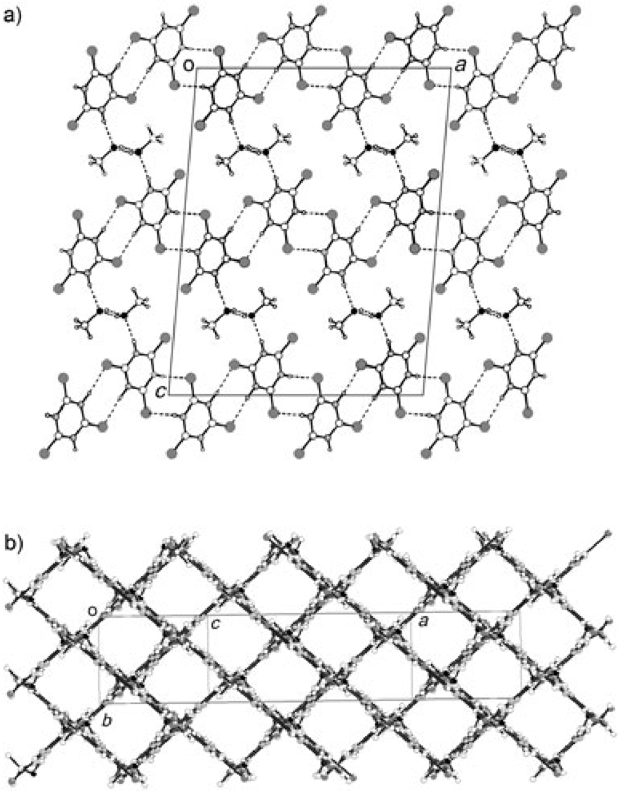


Figure 4. a) Part of the structure of the **TTCA**/methanol co-crystal, viewed along the *b* axis, showing three single-tapes of **TTCA** molecules of type 2. The single-tapes do not lie in the *ac* plane, but run alternately out of the page (bottom and top tapes shown) and into the page (middle tape shown) on moving from left to right along the tape. A methanol molecule is linked to each **TTCA** molecule by an N–H···O hydrogen bond (dashed line). The three single-tapes shown are present in different slabs (see text), and the methanol molecules occupy the region between adjacent slabs. b) Crystal structure of the **TTCA**/methanol co-crystal, viewed perpendicular to the slabs. In the projection shown, the structure resembles an approximately square grid-like arrangement, as discussed in the text.

and the other co-crystals. In particular, the **TTCA**/methanol co-crystal does *not* contain two-dimensional sheets in which adjacent tapes lie in the same plane as each other. Instead, we can consider that the tapes are stacked on top of each other to form a two-dimensional slab, in which the planes of the individual tapes are essentially perpendicular to the plane of the slab. The stacking of tapes to form these slabs is somewhat analogous to the stacking of the two-dimensional sheets in the other co-crystals. However, for **TTCA**/methanol, the relative positions of the **TTCA** molecules in adjacent tapes within the slab is such that some S atoms of one tape lie almost directly above an N atom of the adjacent tape and some S atoms of one tape lie almost directly above the centre of the ring of a **TTCA** molecule in the adjacent tape. The perpendicular distance between adjacent tapes within the slab is about 3.5 Å.

As now discussed, the methanol molecules that are pendant to a given slab play an important role at the interface between adjacent slabs. Thus, adjacent slabs are stacked on top of each other such that, as shown in Figure 4b, the directions of the **TTCA** tapes in adjacent slabs are essentially perpendicular to each other. When viewed in projection perpendicular to the slabs (Figure 4b), this gives the appearance of an approximately square grid-like arrangement of the **TTCA** tapes (the angle formed, in projection, between the tapes in adjacent slabs is about 80°, rather than 90° for a strictly square grid). Importantly, the pendant methanol molecules at the interface between adjacent slabs are engaged in a zig-zag ···O−H···O−H···O−H··· hydrogen bonded chain.[10] Thus, each methanol oxygen atoms acts as a hydrogen bond acceptor to both the N−H bond of a **TTCA** molecule and the O−H bond of another methanol molecule. Alternate methanol molecules along the zig-zag chain receive their N−H···O hydrogen bond from an N−H bond in the **TTCA** slab above and from an N−H bond in the **TTCA** slab below.

Concluding Remarks

We have reported the structural properties of six co-crystals of **TTCA**, obtained by crystallisation of **TTCA** from different solvents with hydrogen bonding functionality. The co-crystals are conveniently classified according to the structural arrangement of the **TTCA** molecules, which comprises either double-tapes or single-tapes (of which there are three distinct types) of **TTCA** molecules. In all structures, the "other" molecule engages in hydrogen bonding interactions involving "free" N−H bonds on the **TTCA** tapes as the hydrogen bond donor. In all co-crystals except **TTCA**/methanol, the "other" molecule behaves only as a hydrogen bond acceptor, and the crystal structures in these cases can be rationalized on the basis of the packing of the **TTCA** tapes with pendant hydrogen bonded solvent molecules. Thus, the formation of single-tapes of type 3 in **TTCA**/acetonitrile in comparison to the formation of single-tapes of type 1 in **TTCA**/DMF and **TTCA**/DMSO can be rationalised on the basis of matching the periodicity of these tapes with the size of the pendant solvent molecule, and the formation of double-tapes in the **TTCA**/acetone and **TTCA**/2-butanone structures can be rationalized on the basis that the double tape structure allows efficient packing of adjacent two-dimensional sheets on top of each other. The co-crystal formed between **TTCA** and methanol introduces additional structural features, arising from the fact that each methanol molecule can participate in hydrogen bonding *both* as a donor and as an acceptor.

Clearly the rationalisation of the structural features of **TTCA** co-crystals established from the present study will serve as a systematic basis for predicting and rationalising the structures of co-crystals formed between **TTCA** and other molecules containing hydrogen bonding functionality.

Experimental Section

Preparation of co-crystals: The co-crystals were prepared by dissolving **TTCA** (Aldrich) in acetone, 2-butanone, dimethyl sulfoxide (DMSO) (or 2:1 DMSO/water), dimethylformamide (DMF) (or 2:1 DMF/water), methanol and acetonitrile (or 2:1 DMF/acetonitrile), and subsequently allowing slow evaporation of solvent from these solutions. The **TTCA**/acetone and **TTCA**/methanol systems yielded single crystals within 24 h, whereas the other systems gave single crystals over a longer time (typically one week). In all cases, good quality crystals suitable for single-crystal X-ray diffraction studies were obtained, but tended to be unstable under ambient conditions, leading to loss of crystal quality over time (with the different co-crystals having different relative stability in this regard).

Structure determination: The structure determination was carried out by using single-crystal X-ray diffraction techniques. Single crystals were glued to the tip of a glass fibre using araldite or a superglue adhesive and mounted on a goniometer head. Because of the susceptibility of the crystals to degradation, the crystals were smeared in araldite to protect them from direct exposure to the atmosphere. Thus, the crystals did not deteriorate during data collection. The intensity data were collected on a Siemens SMART diffractometer[11] equipped with a CCD detector (for the co-crystals with acetone, DMF, 2-butanone and methanol), an Enraf-Nonius CAD4 diffractometer (for the co-crystal with DMSO) and on a Rigaku R-axis IIc diffractometer equipped with an image plate detector system and Mo rotating anode source (for the co-crystals with acetone, DMSO, DMF, 2-butanone and acetonitrile). For those materials studied on more than one instrument, the structure determination results were in good agreement, and in such cases the structural data considered to be of higher quality are presented. All data collections used $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and were carried out at ambient temperature (293 K). No absorption corrections were applied. Structure solution and refinement were carried out using the SHELXTL-PLUS suite of programs,[12] with refinement carried out by full-matrix least-squares on F^2. In all cases, the structure determination calculations were straightforward. Crystallographic details for all co-crystals are summarized in Table 1. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were refined using isotropic displacement parameters (starting from peak positions established from difference Fourier maps) for all co-crystals except **TTCA**/methanol and **TTCA**/acetonitrile (for which the hydrogen atoms were placed in calculated positions). All hydrogen bond lengths were determined using the program PLATON.[13] Selected details of the hydrogen bond geometries are given in the Crystallographic data.

CCDC-234879–CCDC-234883 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from

Table 1. Relevant crystallographic data for the **TTCA** co-crystals discussed in the text.

	TTCA/acetone	**TTCA**/dimethyl sulfoxide	**TTCA**/dimethylformamide	**TTCA**/2-butanone	**TTCA**/methanol	**TTCA**/acetonitrile
formula	$2(C_3H_3N_3S_3)\cdot C_3H_6O$	$C_3H_3N_3S_3\cdot C_2H_6OS$	$C_3H_3N_3S_3\cdot C_3H_7ON$	$2(C_3H_3N_3S_3)\cdot C_4H_8O$	$C_3H_3N_3S_3{:}CH_4O$	$C_3H_3N_3S_3{:}C_2H_3N$
molar mass [g mol^{-1}]	412.61	255.39	250.36	426.64	209.31	218.32
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$		$C2/c$	$P2_1/m$
a [Å]	8.945(1)	4.666(1)	9.789(1)	10.130(2)	17.472(3)	5.266(2)
b [Å]	9.999(1)	10.423(1)	12.763(1)	10.358(2)	4.611(1)	8.814(1)
c [Å]	10.464(1)	11.777(2)	9.285(1)	9.606(1)	22.593(4)	10.525(3)
α [°]	95.14(1)	85.39(1)	90	99.33(1)	90	90
β [°]	96.78(1)	87.73(1)	91.19(1)	110.53(1)	94.96(1)	102.70(1)
γ [°]	107.29(1)	78.58(1)	90	90.57(2)	90	90
Z	2	2	4	2	8	2
V [Å^3]	879.7(2)	559.4(2)	1159.8(2)	929.0(2)	1813.4(6)	476.5(2)
ρ_{calcd} [Mg m^{-3}]	1.558	1.516	1.434	1.525	1.533	1.521
no. of reflections	3422	2190	4389	5701	3247	2330
no. of unique data	2441	1555	1663	3010	1294	317
data with $I > 2\sigma$	2433	1351	1069	2884	835	313
R_1	0.035	0.033	0.053	0.038	0.054	0.075
$wR2$	0.090	0.084	0.119	0.093	0.089	0.198
Goof	1.02	1.04	1.19	1.11	1.22	1.18

The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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