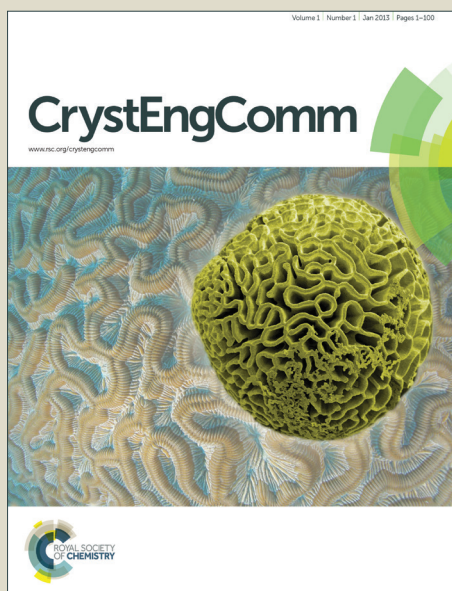


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# Self-Assembly of Sterically-Rigidified 3-Connecting Benzenetribenzoic Acid into (6,3) and (3,3) Nets and Stabilization of Water Channel in the Crystal Lattice

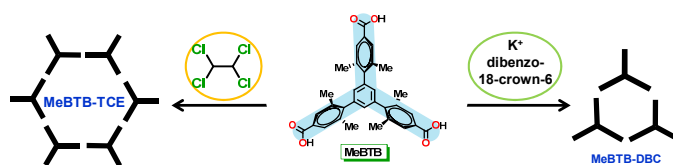
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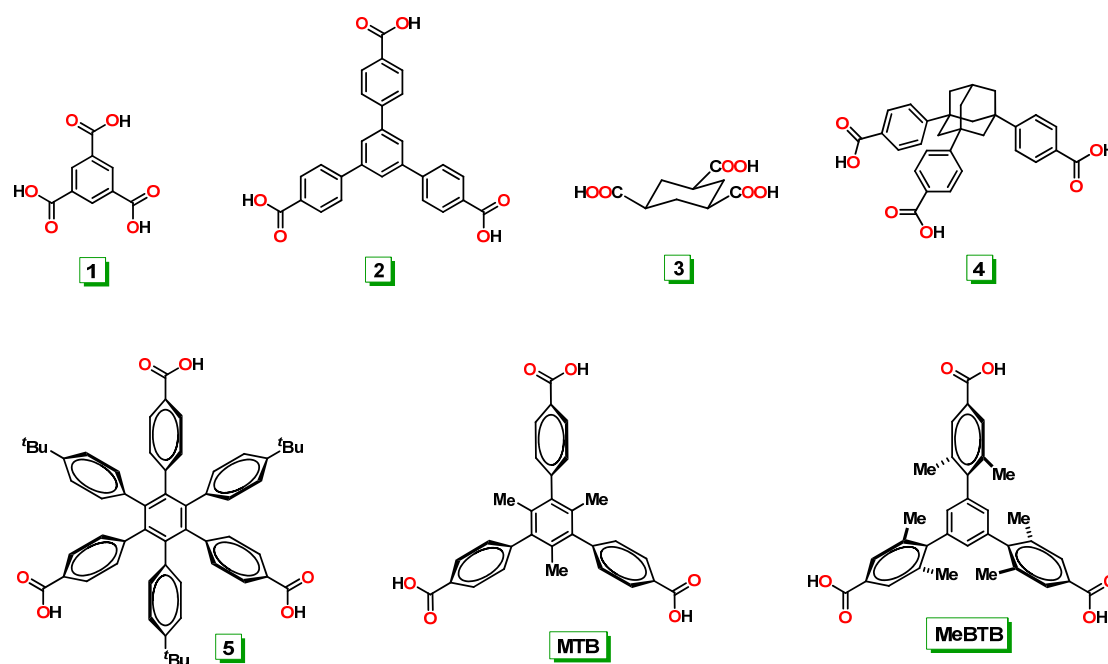
## ABSTRACT

A rigid 3-connecting triacid **MeBTB** was designed and synthesized in quest of guest inclusion in the pores of honeycomb network structures generated based on the acid dimer-mediated self-assembly. Crystallization of **MeBTB** is indeed found to lead to a (6,3) net that is 3-fold interpenetrated. Charge-assisted hydrogen bond-mediated self-assembly in the presence of KX/dibenzo-18-crown-6 is likewise found to lead to a (3,3) honeycomb net, which is also 3-fold interpenetrated. When contrasted with the results of self-assembly of sterically-unhindered 1,3,5-benzenetribenzoic acid **2** and those of analogous tribenzoic acid based on mesitylene, that is **MTB**, the sterics built into the structure of **MeBTB** allow engineering of ordered assemblies with reduced interpenetration and higher solvent-accessible volumes. The limited, yet a meaningful number of structures demonstrates the fact that the rigid building blocks, while responding to the expectations based on aggregation via acid dimer synthon, are most likely to present rich diversity in terms of synthon adoptions and spring up surprises in the self-assembly through inclusion of adventitious water. Crystallization of **MeBTB** in MeOH-DME led to a disappearing solvate form in which the helically organized acids are found to sustain a water channel.

## INTRODUCTION

The strength and directionality associated with O/N–H···O/N hydrogen bonds are invaluable in organizing molecules in a predefined manner.<sup>1</sup> As the solid state bulk properties depend on organization of the constituent molecules, the latter can be rationally programmed in a bottom-up approach to engineer solid state properties.<sup>2</sup> In this regard, the carboxylic acid functional group has played a pivotal role in the development of molecular self-assembly in general.<sup>3</sup> The acids undergo aggregation predominantly by adopting either of the two homomeric synthons, namely dimer and catemer. The former involving two O–H···O hydrogen bonds is a very reliable supramolecular synthon for predictive organization of molecules. It has been successfully employed to create diverse zero- to multidimensional network structures in the solid state.<sup>3</sup> There has been particular interest in 3-connecting triacids, as they permit realization of porous honeycomb structures not only in the solid state,<sup>4</sup> but also on liquid-solid interfaces.<sup>5</sup> It turns out that trimesic acid **1** represents a prototype example, which self-assembles in the solid state as well as on the surface into a honeycomb network. In the solid state, the (6,3) net has been found to undergo interpenetration,<sup>6</sup> which can be disrupted in the presence of suitable guest molecules that occupy the void spaces.<sup>4b,7</sup> In Figure 1 are shown various 3-connecting trigonal triacids, whose self-assembly based on dimer motif of the acids into honeycomb structures has been explored. 1,3,5-Benzenetribenzoic acid **2** is an enlarged analog of trimesic acid, whose self-assembly may lead to pores of the dimension of ca. 28 Å as revealed by microscopic studies on solid surfaces.<sup>8</sup> Curiously, the crystal structure of **2** with a honeycomb network is heretofore unknown, while lattice inclusion of DMSO that terminates the hydrogen bond-mediated aggregation has been documented.<sup>9</sup> 1,3,5-*cis*-Cyclohexanetricarboxylic acid **3** has been shown to form a perfect honeycomb network with 18-crown-6 occupying the void spaces as a guest.<sup>10</sup> The

rigid and tripodal adamantanetribenzoic acid **4** has been shown to lend itself to the observation of Borromean network via interdigitation of undulated (6,3) nets resulting from the self-assembly based on the dimer motif.<sup>11</sup> In a sterically-rigidified triacid **5** based on hexaarylbenzene, inclusion of adventitious water has been shown to lead to an unusual supramolecular synthon that mediates the self-assembly.<sup>12</sup> In our own early investigations, we found that the dimer synthon is not necessarily reproduced in the crystal structures of highly rigid acids; indeed, simple halogen substitution<sup>13a</sup> and tethering<sup>13b</sup> have been found to divert the molecular self-assembly based on dimer synthon.



**Figure 1.** Various 3-connecting trigonal triacids, whose self-assembly based on dimer motif of the acids into honeycomb structures has been reported in literature.

Against the above literature background, we sought to explore the self-assembly of sterically-rigidified 3-connecting triacids based on mesitylene and benzene cores, i.e., 1,3,5-tris(4-



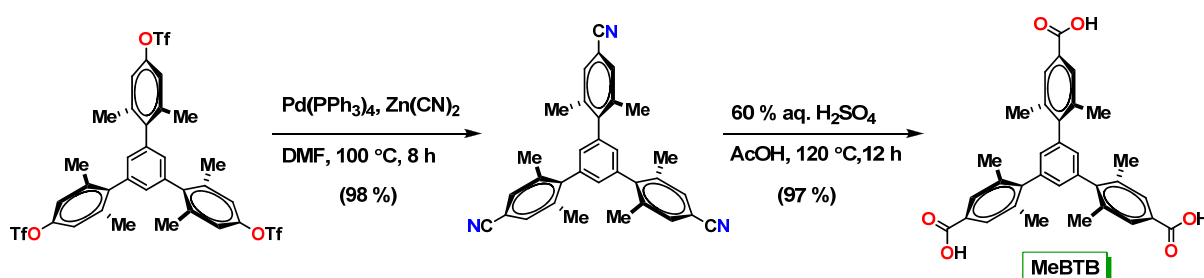
carboxyphenyl)mesitylene **MTB**<sup>14</sup> and 1,3,5-tris(2,6-dimethyl-4-carboxyphenyl)benzene (**MeBTB**). Although both triacids are similar in terms of their arm lengths, they differ vastly in the following: i) the void spaces created by the self-assembly of **MTB** should be expected to be smaller due to methyl groups of the mesitylene core, which protrude into the pores, and ii) the dimethyl groups that lie near-orthogonally to the central benzene ring in **MeBTB** should increase the thickness of the pores generated by self-assembly. We recently showed that the triacid **MTB** does indeed undergo acid dimer-mediated self-assembly into a (6,3) net with pores of ca. 24-26 Å diameter and that its crystallization in the presence of KX/18-crown-6 or dibenzo-18-crown-6 leads to charge-assisted hydrogen bond-mediated self-assembly into honeycomb networks nesting K<sup>+</sup>-bound crowns in the pores thus generated.<sup>14</sup> Herein, we report our results on the self-assembly of triacid **MeBTB**. It is shown that the latter crystallizes in different crystal forms depending on the solvent of crystallization; while the anticipated molecular organization involving (6,3) net with 3-fold interpenetration is observed in one with ca. 56% solvent-accessible volume, a unique helical organization that sustains a water channel is observed in the other. Further, crystallization in the presence of KX/dibenzo-18-crown-6 is shown to occur leading to a (3,3) net with pore dimensions large enough to accommodate K<sup>+</sup>⊂dibenzo-18-crown-6.

## RESULTS AND DISCUSSION

**Synthesis of MeBTB.** The synthesis of **MeBTB** was accomplished starting from the precursor triphenol, which was converted to its tritriplate; syntheses of both triphenol and its triplate have previously been reported by us.<sup>15</sup> The triplate was conveniently converted to the corresponding

cyanide with  $\text{Zn}(\text{CN})_2$  in DMF under  $\text{Pd}(0)$ -catalyzed conditions, and the resultant trinitrile was hydrolyzed to afford the required triacid **MeBTB** in a respectable overall yield.

**SCHEME 1.** Synthetic protocol for the preparation of **MeBTB**.



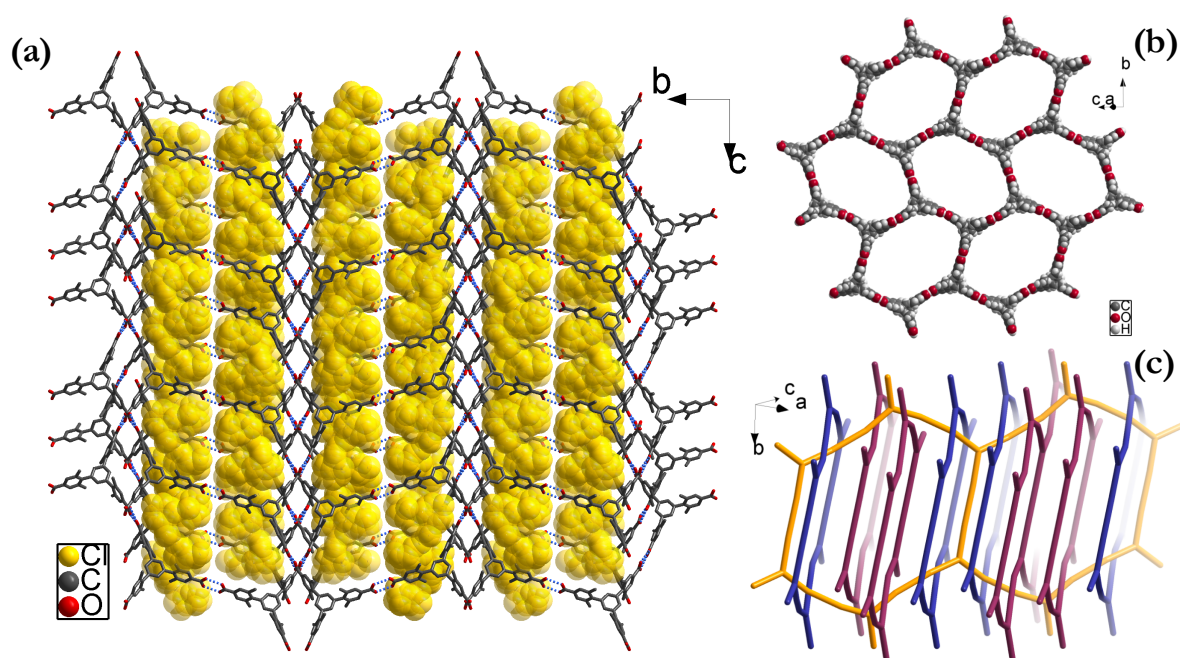
**Self-Assembly of Trigonal MeBTB in the Solid State.** In a number of crystallization experiments, **MeBTB** was found to crystallize in DME-MeOH and tetrachloroethane-MeOH mixture as needle- (**MeBTB**-DME) and prism-shaped (**MeBTB**-TCE) crystals, respectively. Crystallization of **MeBTB** by slow evaporation of its solution in DME-MeOH mixture in the presence of dibenzo-18-crown-6 and potassium acetate led to cubic crystals (**MeBTB**-DBC). Suitable crystals in each case were subjected to X-ray intensity data collection and subsequent crystal structure determinations. In Table 1 are collected crystal data for the three structures determined. In the following, the structural analyses are described for each case and a gist of the findings is consolidated toward the end.

**Table 1.** The crystal data for inclusion and multicomponent crystals of host **MeBTB** with various guests

compound	MeBTB-TCE <sup>a</sup>	MeBTB-DME	MeBTB-DBC
Molecular formula	C <sub>33</sub> H <sub>30</sub> O <sub>6</sub> •2C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	2C <sub>33</sub> H <sub>30</sub> O <sub>6</sub> •2C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> •2H <sub>2</sub> O	C <sub>33</sub> H <sub>28.5</sub> O <sub>6</sub> •K <sub>1.5</sub> •2C <sub>20</sub> H <sub>24</sub> O <sub>6</sub> •2H <sub>2</sub> O
Formula weight	858.28	1261.44	1336.52
Temperature (K)	100(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Hexagonal	Monoclinic
Space group	<i>Pbca</i>	<i>P6<sub>1</sub></i>	<i>P2<sub>1</sub></i>
a (Å)	50.850(16)	25.350(4)	8.6821(8)
b (Å)	15.260(5)	25.350(4)	29.796(3)
c (Å)	14.006(4)	18.979(4)	12.8045(12)
α (°)	90	90	90
β (°)	90	90	96.43(1)
γ (°)	90	120	90
Volume (Å <sup>3</sup> )	10868(6)	10562(3)	3291(1)
Z	8	6	2
Calculated density (mg/m <sup>3</sup> )	1.049	1.190	1.349
Absorption coefficient (mm <sup>-1</sup> )	0.446	0.085	0.189
F(000)	3520	4032	1414
θ range for data collection (°)	1.56 to 25.00	1.93 to 25.00	1.60 to 25.00
Index ranges	-41 ≤ k ≤ 60 -18 ≤ h ≤ 18 -14 ≤ l ≤ 16	-30 ≤ h ≤ 25 -29 ≤ k ≤ 30 -21 ≤ l ≤ 22	-10 ≤ h ≤ 10 -35 ≤ k ≤ 34 -15 ≤ l ≤ 10
Reflections collected	53389	55064	17091
Independent reflections	9426 [Rint = 0.1341]	12237 [Rint = 0.0633]	10384 [Rint = 0.0548]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraint/parameters	9426/0/352	12237/55/817	10384/47/856
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.014	1.060	1.073
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R <sub>1</sub> = 0.0817, wR <sub>2</sub> = 0.1768	R <sub>1</sub> = 0.0728, wR <sub>2</sub> = 0.1768	R <sub>1</sub> = 0.0710, wR <sub>2</sub> = 0.1380
R indices (all data)	R <sub>1</sub> = 0.1634, wR <sub>2</sub> = 0.1970	R <sub>1</sub> = 0.1038, wR <sub>2</sub> = 0.1948	R <sub>1</sub> = 0.1106, wR <sub>2</sub> = 0.1556

<sup>a</sup> The data correspond to the structure refined with squeeze option. Without squeeze option employed, some of the refinement values are as follows: independent reflections 9426 [Rint = 0.1486]; data/restraint/parameters 9426/128/548; Goodness-of-fit on *F*<sup>2</sup> 1.672; Final R indices [*I* > 2σ(*I*)] R<sub>1</sub> = 0.1833, wR<sub>2</sub> = 0.4279; R indices (all data) R<sub>1</sub> = 0.2673, wR<sub>2</sub> = 0.4562.

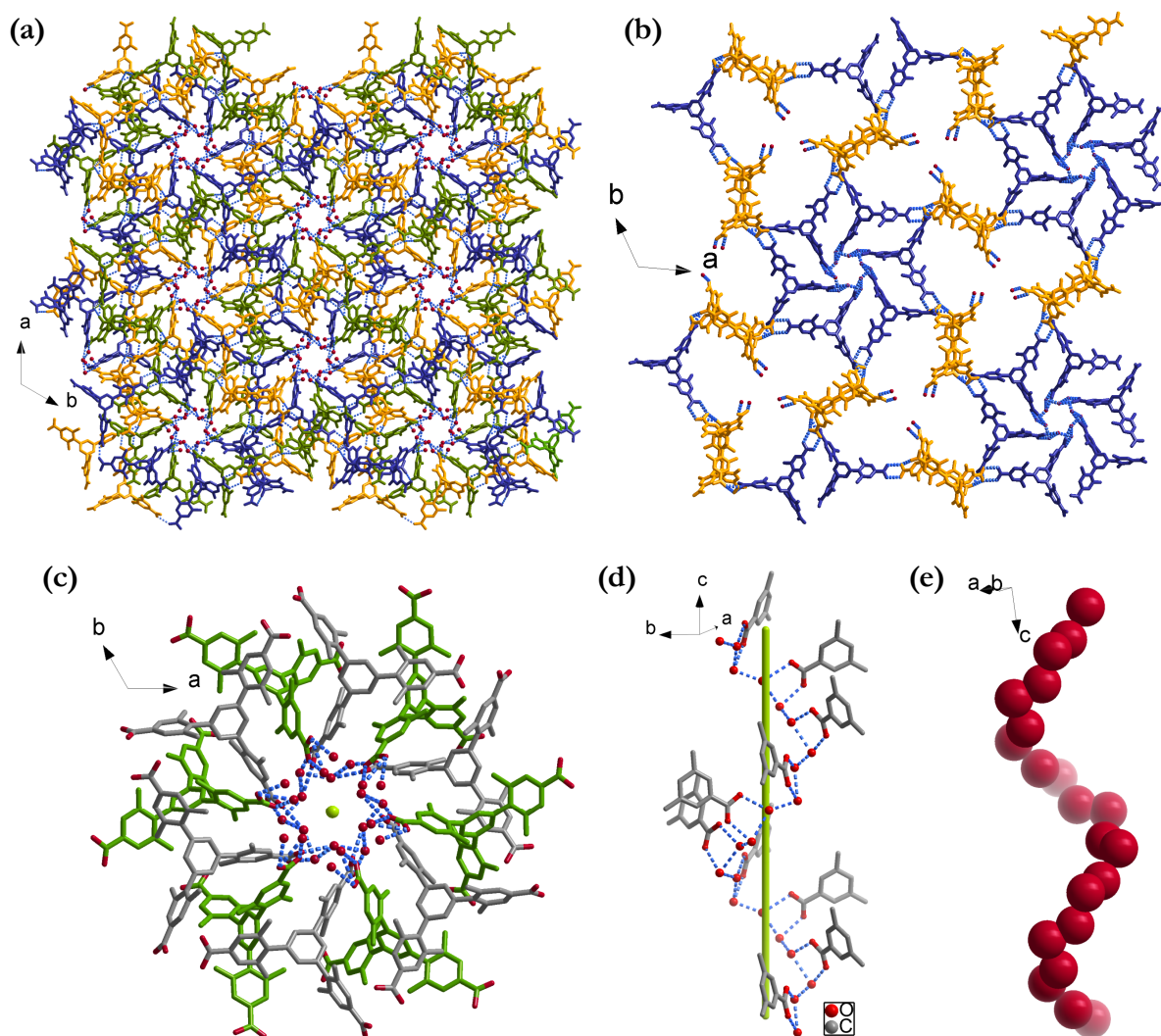
Crystallization of **MeBTB** in a 1,1,2,2-tetrachloroethane-MeOH (1:1, v/v) mixture via slow evaporation over a period of two weeks led to large prism-shaped crystals. The crystals were found to belong to *Pcab* space group. The crystal structure analyses revealed that the 3-connecting rigid triacid undergoes hexameric association via acid dimer synthon leading to a 2-dimensional (6,3) net. The resultant honeycomb structure, shown in Figure 2b, contains huge voids with cavity dimensions of the order of 26-28 Å in diameter. The space group symmetry of the crystals brings about 3-fold inclined interpenetration of the network such that close packing is achieved, Figure 2. The solvent, that is, two equivalents of tetrachloroethane, is found to fill the void spaces that still remain in the crystal lattice, Figure 2a. The calculated solvent-accessible volume is ca. 56%.



**Figure 2.** (a) The overall crystal packing of **MeBTB-TCE** showing tetrachloroethane guest species (yellow) in the network structure. (b) Acid dimer-mediated assembly of MeBTB into a 2D honeycomb layer. (c) 3-Fold inclined interpenetration of the 2D layers.

The crystals of **MeBTB** crystallized from dimethoxyethane (**MeBTB**-DME) were found to belong to the chiral  $P6_1$  space group. The structure determination revealed that the asymmetric unit cell contains two molecules each of the triacid **MeBTB**, DME and water. In both independent triacids, referred to as A and B, the carboxyphenyl rings are found to be oriented with respect to the central benzene ring at an angle of 71-73°. The crystal packing analyses reveal that one carboxylic acid of A is connected to one carboxylic acid of B via dimer motif, while two acids of A and B are found to associate in a truncated *syn*-catemer fashion, Figure 3a; while one COOH is hydrogen bonded to the carbonyl of the other, the hydrogen of the latter is found to be bonded to the disordered dimethoxyethane solvent molecule. This leaves us with one carboxylic acid each for the two independent triacids A and B. In both A and B, the third carboxylic acid is found to be hydrogen bonded to a discrete water molecule that terminates hydrogen bond-mediated propagation. In both cases, the water molecule is found to be disordered at two positions such that it is hydrogen bonded to both oxygens of carboxylic acid group implying thereby that the hydrogen of the acid is also disordered likewise about the two oxygens. A closer inspection of the packing reveals that six molecules of **MeBTB** are arranged about the  $6_1$ -screw axis such that the carboxylic acid hydrogens bonded to water molecules are helically connected, Figure 3. Thus, the propagation down c-axis leads to an unusual water channel stabilized by helically organized carboxylic acids. In other words, while the catemeric motif between molecules A and B ensures propagation of two independent triacids in the ab-plane, the water channel propagates down c-axis leading to a 3-dimensional molecular packing. Further analysis shows that two DME molecules are hooked on to the dimer formed between molecules A and B via the truncated catemeric motif. This crystal structure is unique in the sense

that one observes dimer as well as truncated catemer synthons of the acid in the crystal lattice in addition to the synthon involving COOH group terminated by water.

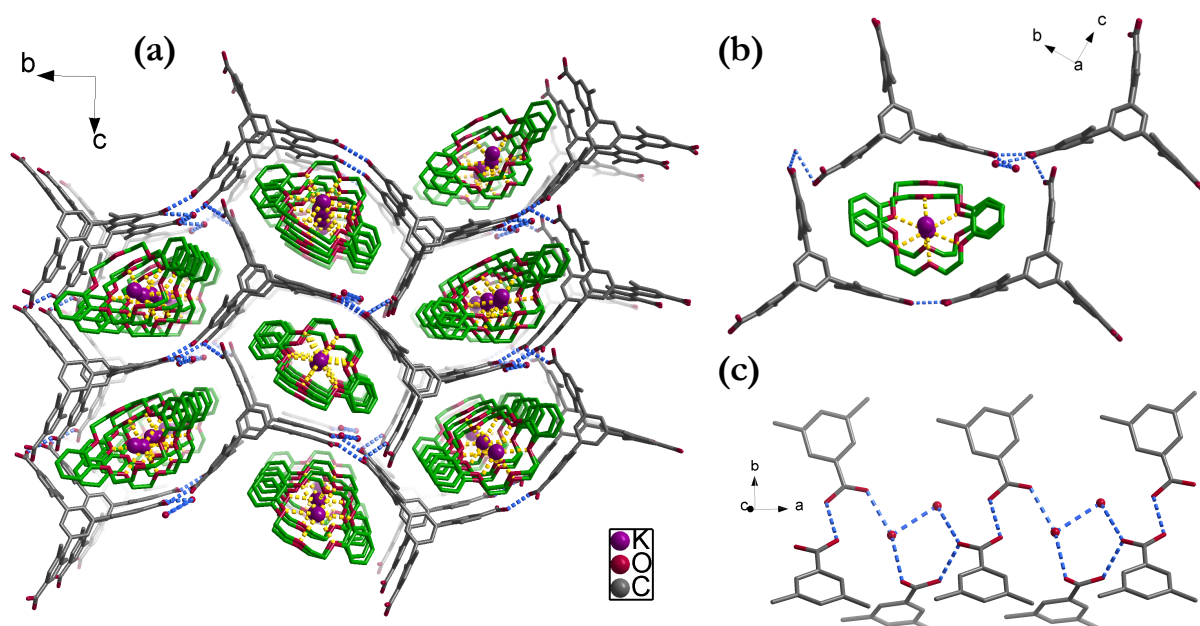


**Figure 3.** (a) The crystal packing diagram of **MeBTB-DME**; note that DME molecules have been omitted for clarity. (b) Hydrogen bond-mediated propagation of two independent molecules in the asymmetric unit cell connected by the acid dimer motif is shown separately for clarity. (c) The helical organization of molecules that sustain the disordered water channel. (d and e) For clarity, the disordered water in the channel stabilized by the acid functionalities via hydrogen bonds is shown separately.



The crystal structure analysis of **MeBTB**-DBC showed that the asymmetric unit cell contains one molecule of **MeBTB**, 1.5 equivalents of  $K^+$  ion, 2 molecules of dibenzo-18-crown-6 and 2 molecules of water. While one of the  $K^+$  ions is found to be bound to one dibenzocrown, the other  $K^+$  ion is found to be bound to the second dibenzocrown with a probability of 50%. This also implies that three carboxylic acid groups of every two **MeBTB** molecules must necessarily undergo deprotonation to compensate the charges of  $K^+$  ions. It should be emphasized that the hydrogen atoms of the carboxylic acids could not be readily located from the difference Fourier.

The molecular packing in the multicomponent crystals of **MeBTB** with  $K^+$  ions bound to the dibenzocrowns is shown in Figure 4. As may be seen, three molecules of **MeBTB** related by 2<sub>1</sub>-screw and translational symmetry (along c-axis) are connected by an array of O–H···O hydrogen bonds as well as charge-assisted hydrogen bonds<sup>4d,e,16</sup> down a-axis; as mentioned earlier, the ambiguity associated with the location of the hydrogen atoms of the carboxyl groups renders distinction between moderate O–H···O hydrogen bonds and charge-assisted strong hydrogen bonds difficult. Otherwise, the hydrogen bonded aggregation of the partially deprotonated **MeBTB** may be analyzed based on O···O distances. Thus, the hydrogen bonded aggregation of the trigonal **MeBTB** acids leads to a layered honeycomb structure in the bc-plane with significant void spaces generated by the assembly of three host molecules. The crystal structure analyses reveal a 1-dimensional O–H···O hydrogen bonded synthon (Figure 4c) as being responsible for the observed aggregation; the two water molecules found in the asymmetric unit cell are seen to mediate the hydrogen bonded aggregation, as the latter propagates down a-axis, the honeycomb layers are connected such that one observes a 3-D structure with channels down a-axis. The  $K^+$ -bound dibenzocrowns are found to be nicely accommodated within the channels leading to a multicomponent crystal.<sup>17</sup>



**Figure 4.** (a) The crystal packing diagram of **MeBTB**-dibenzo-18-crown-6. (b) The trimeric hydrogen bonded assembly nesting  $K^+$ -dibenzocrown. (c) The water-mediated hydrogen-bonded synthon that enables 3-dimensional propagation of the otherwise 2-dimensional honeycomb network.

**Influence of Sterics on the Hydrogen Bond-Mediated Self-Assembly of MeBTB.** The 3-connecting trigonal molecular building blocks, the prototype of which is trimesic acid, have long offered excitement from the point of view of creating ordered 2-dimensional aggregates.<sup>4,5</sup> While the literature is abound with respect to the self-assembly of trimesic acid into (6,3) honeycomb nets that include a variety guest species,<sup>4b,6,7</sup> attempts at realizing analogous 2-dimensional open network structures with its extended derivative, namely 1,3,5-benzenetribenzoic acid **2**, have been noted to have met with failure.<sup>9</sup> Indeed, our own attempts were to no avail.<sup>14</sup> Our recent investigations on the sterically-hindered analog based on mesitylene core, that is, **MTB** in Figure



1, led to demonstration of the fact that the rigid molecular building block permits expected self-assembly into a (6,3) net with pores of the dimensions of ca. 24-26 Å.<sup>14</sup> However, the 2D-network was found to undergo 6-fold inclined interpenetration with inclusion of dimethoxyethane in the void spaces that still remain. The charge-assisted self-assembly of the monodeprotonated triacid **MTB** in the presence of dibenzo-18-crown-6/KOAc was also demonstrated to lead to water-expanded (6,3) net, which is again 6-fold interpenetrated.<sup>14</sup> For comparison, **MeBTB** host designed and investigated herein differs from the fact that the central benzene core is devoid of methyl groups that otherwise occupy the pores resulting from aggregation as in **MTB**. Further, the two methyl groups meant to ensure orthogonality with respect to the central core impart depth to the pores.

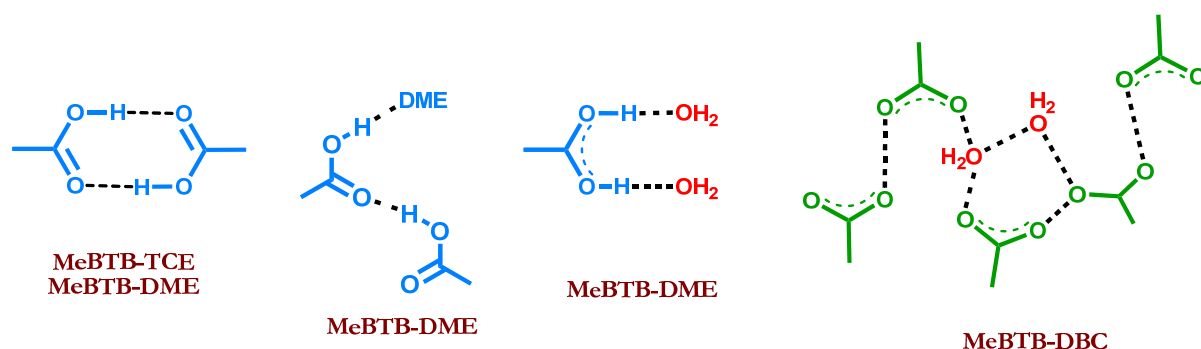
Structural analyses of the crystals of **MeBTB** grown in the presence of tetrachloroethane show that the self-assembly leads to a (6,3) net as anticipated with pore dimensions of the order of 26-28 Å. Remarkably, it is 3-fold interpenetrated in contrast to that of **MTB**. PLATON analyses reveal that the solvent accessible volume is as high as ca. 56% when compared to ca. 44% in **MTB** crystals that are 6-fold interpenetrated. Thus, the analogous structures exhibit similar organization, but with different magnitudes of self-interpenetration and guest-accessible volume. In the same manner, while **MTB** has been found to undergo charge-assisted aggregation into a (6,3) net that is 6-fold interpenetrated in the presence of dibenzo-18-crown-6/KOAc via acid dimer and water-mediated carboxyl...carboxyl synthons,<sup>14</sup> **MeBTB** in the present instance is found to undergo aggregation via mediation of water into a (3,3) net with the pores nesting the K<sup>+</sup>⊂dibenzocrown. PLATON analyses reveal that the solvent-accessible volume in this instance is ca. 53% when K<sup>+</sup>⊂dibenzocrown is excluded. Clearly, diligent exploitation of sterics and rigidity in the molecular design allows engineering of ordered assemblies and with reduced

interpenetration when contrasted with the results observed for 1,3,5-benzenetribenzoic acid **2** and **MTB**, Figure 1.

The crystallization of **MeBTB** in DME is found to lead to a unique assembly involving dimer and truncated catemeric synthons of the carboxylic acid in addition to inclusion of adventitious water. In the lattice, the helical organization of carboxyl groups is found to stabilize disordered helical water channel, Figure 3; the literature reveals a few instances of water helical chains stabilized in the crystals by lattice forces.<sup>18</sup> It must be mentioned that growth of these crystals could not be reproduced from several experiments. Given that the hydrates constitute 8% of the crystal structures known,<sup>19</sup> the question of why and when inclusion of adventitious water occurs is important in the context of crystal engineering, which is concerned with achieving predefined properties via controlled molecular organization. The observed results prompt one the following questions: How often are the catemeric as well as dimer synthons observed in the crystal structures of acids? Given that the acid dimer motif is believed to be the robust one,<sup>3</sup> why does one begin to observe departure from the observation of this synthon? The answers to these questions appear to be traceable to the molecular features inherent to **MeBTB**. Seemingly, the sterically-hindered and rigid building blocks appear to be highly 'sensitive' systems, which inherently exhibit packing difficulties; by the word 'sensitivity', we mean that the sterically-rigidified molecular systems exhibit tendency to undergo departure from adoption of the preferred supramolecular synthons with subtle experimental perturbations. We have shown earlier that weak interactions due to the presence of certain groups such as halogens and tethering in dicarboxylic acids modify the otherwise favored adoption of dimer synthon in sterically-hindered carboxylic acids.<sup>13</sup>

Inclusion of adventitious water is observed in the crystals of **MeBTB**-DME and **MeBTB**-DBC, and it appears to owe its origin to the packing difficulties; of course, inclusion of water fills the void spaces in the lattice and enables close packing.<sup>20</sup> Presumably, the packing difficulties that arise as a consequence of adoption of favored synthons are overcome when the molecules explore alternative motifs of aggregation forged by adventitious water, which fills the void spaces in the crystal lattice. This indeed is supported by some results of our own investigations. We reported some time ago that inclusion of planar water hexamer was serendipitously observed in the crystals of sterically-hindered bimesitylenedicarboxylic acid.<sup>21</sup> Inclusion of water was also noted in some tethered diacids.<sup>22</sup>

Insofar as the supramolecular synthons observed in the crystal structures are concerned, one observes rich diversity in the limited crystal structures; while the regular dimer synthon is observed in **MeBTB**-TCE, a rare simultaneous occurrence of dimer and truncated catemer synthons<sup>23</sup> along with water-terminated acid synthon is observed in **MeBTB**-DME, Figure 5. Further, a 1D carboxyl...carboxylate synthon expanded by two water molecules is observed in **MeBTB**-DBC. Clearly, the results suggest that the rigid molecular building blocks, while responding to the expectations based on aggregation via acid dimer synthon, present rich diversity in synthon adoptions by the carboxylic acids. The charge-assisted self-assembly of partially-deprotonated polyacids such as **MeBTB**-DBC should be very exciting from the point of view of observation of new synthons and addressing the issue of water inclusion in crystals, for they correspond to systems with poor hydrogen bond donor-acceptor ratios. Thus, they will most likely include adventitious water in pursuit of improving the ratio and achieving close packing.<sup>24</sup>



**Figure 5.** Various supramolecular synthons (dimer, truncated catemer, disordered water-terminated acid, 1D-chain) observed in the crystal structures of **MeBTB-TCE**, **MeBTB-DME** and **MeBTB-DBC**.

## CONCLUSIONS

We have designed, synthesized and investigated carboxylic acid dimer-mediated self-assembly of a novel sterically-hindered and rigid 3-connecting triacid **MeBTB** in quest of guest inclusion via formation of porous honeycomb networks. The triacid **MeBTB** is indeed found to exploit the acid dimer motif when crystallized in tetrachloroethane and self-assemble into a (6,3) net, which is 3-fold interpenetrated with significant solvent-accessible volume in contrast to 6-fold interpenetration observed in the analogous triacid **MTB**. However, crystallization in the presence of DME was found to lead to a disappearing solvate form in which water channel stabilized by helically organized carboxylic acids is found. Crystallization in the presence of  $K^+$ /dibenzo-18-crown-6 is found to lead to charge-assisted hydrogen bond-mediated assembly sustained by water into a (3,3) net; of course, one of the COOH groups of the triacid is found to undergo deprotonation such that carboxyl...carboxylate supramolecular synthons mediate the self-assembly. Given that the inclusion chemistry is simply not observable with the sterically-

unhindered triacid **2**, the influence of rigidity engineered via sterics exerted by methyl groups is compellingly evident from the results observed herein with **MeBTB**. With limited crystal structures, it emerges that sterically-rigidified acids, while responding to the expectations in terms of dimer synthon adoption, are most likely to spring up surprises in the self-assembly through inclusion of adventitious water.

**Electronic supplementary information (ESI) available.** Experimental details for the preparation of **MeBTB**, details of X-ray crystal structure determinations, geometrical parameters for important O-H...O hydrogen bonds, TGA plots and NMR spectra. The CCDC codes of the structures are: 974555-974557.

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