Abstract: Halogen bonding is one of the most interesting noncovalent attractions capable of self-assembly and recognition processes in both solution and solid phase. In this contribution, we report on the formation of two solvates of tetrabromoterephthalic acid (H$_2$Br$_4$tp) with acetonitrile (MeCN) and methanol (MeOH) viz. H$_2$Br$_4$tp·2MeCN (1MeCN) and H$_2$Br$_4$tp·2MeOH (2MeOH). The host structures of both 1MeCN and 2MeOH are assembled via the occurrence of simultaneous Br···Br, Br···O, and Br···π halogen bonding interactions, existing between the H$_2$Br$_4$tp molecular tectons. Among them, the cooperative effect of the dominant halogen bond in combination with hydrogen bonding interactions gave rise to different supramolecular assemblies, whereas the strength of the halogen bond depends on the type of hydrogen bond between the molecules of H$_2$Br$_4$tp and the solvents. These materials show a reversible release/resorption of solvent molecules accompanied by evident crystallographic phase transitions.

Keywords: halogen bonds; hydrogen bonds; solvate; structural phase transition; Hirschfeld surface; tetrabromoterephthalic acid

1. Introduction

Supramolecular interactions have been extensively investigated due to their importance in governing various interesting physical properties as well as chemical and biological assemblies [1–3]. Halogen bonding (XB) is emerging as one of the prominent intermolecular interactions that takes place between the sigma (σ)-hole of the polarizable halogen atom (Lewis acid, XB donor) and the electron-rich atom or π-electron system (Lewis base, XB acceptor) [4,5]. Generally, the XB interaction is presented as D···Y···A, where D···Y and A are the XB donor and XB acceptor, respectively. This type of interaction is highly directional and exhibits highly predictable bond geometries in the solid state. Theoretical calculations have suggested that the strength of the halogen bonding interaction energies is comparable to that of the ubiquitous hydrogen bond [6] and that the strength of the XB donor increases in the following order as the XB donor ability increases: F < Cl < Br < I [7]. These features suggest that the halogen bonding interactions could be used as a crystal engineering tool for designing and developing novel functional materials in the crystalline state [8].

Recently, halogen bond-based supramolecular synthons have been used to construct an exciting class of porous organic materials named halogen-bonded organic frameworks (XBOFs), which are self-assembled from pure organic building blocks (tectons) [9–11]. Compared with analogous materials such as covalent organic frameworks (COFs) and
metal-organic frameworks (MOFs), where the frameworks are built using strong covalent bonds [12], the extended supramolecular frameworks of XBOFs are even more flexible, allowing the inclusion of guests with specific intermolecular interactions. In this regard, the combination of suitable molecular tectons and specific halogen bond synthons is important for the creation of new functional XBOF materials with specific applications. Among the various organic tectons, iodobenzene derivatives and pyridine moieties are the most widely studied in directing the formation of XBOF structures through strong and directional I⋯N synthons [13–15]. For instance, the group of B. Ji and D. Deng recently used the molecular tectons of 1,4-difluoro-2,3,5,6-tetraiodobenzene and 1,2,4,5-tetra(4-pyridyl)benzene to construct a series of XBOFs [16]. The crystal structure determination revealed that the strong and directional I⋯N interactions (3.002 and 3.096 Å) between the respective components is mainly responsible for the formation of flexible frameworks, possessing large flexible breathing 1D channels. Notably, the flexible frameworks of these materials show selective recognition for aromatic guest molecules.

In this work, the tetrabromoterephthalic acid (H$_2$Br$_4$tp) was employed as a molecular building block to synthesize new solvate crystals. This molecule contains two carboxyl and four bromo groups with versatile tectons in self-complementary XB modules bearing both XB donor and XB acceptor sites. Crystallization of H$_2$Br$_4$tp from acetonitrile (MeCN) and methanol (MeOH) yielded two solvates with a 1:2 molar ratio viz. H$_2$Br$_4$tp·2MeCN ($1_{\text{MeCN}}$) and H$_2$Br$_4$tp·2MeOH ($2_{\text{MeOH}}$). As expected, the functional groups of the H$_2$Br$_4$tp tectons can be involved in self-complementary Br···Br, Br···O, and Br···π halogen bonding interactions, resulting in the formation of 2D XBOFs. Moreover, the 2D assemblies can form the inclusion of solvents MeCN and MeOH assembled through both strong and weak hydrogen bonding interactions. These materials can undergo many cycles of release/resorption of solvent molecules, exhibiting crystallographic phase changes between the solvated ($P$-1 for $1_{\text{MeCN}}$ and $P2_1/c$ for $2_{\text{MeOH}}$) and unsolvated ($C2/m$ for H$_2$Br$_4$tp [17]) crystals.

2. Experimental Setup

2.1. Materials and Methods

All chemicals and solvents, i.e., H$_2$Br$_4$tp, MeCN, and MeOH, were reagent grade and were used without further purification. Elemental (C, H, and N) analysis was determined with a LECO CHNS 932 elemental analyzer. Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 ADVANCE X-ray powder diffractometer using Cu Kα ($\lambda = 1.5418$ Å). FT-IR spectra were recorded on a Perkin-Elmer model Spectrum GX FT-IR spectrometer using attenuated total reflection (ATR) mode in the range of 650–4000 cm$^{-1}$. Thermogravimetric analyses (TGA) were carried out using a Metter Toledo TGA/DSC3+ from 30–500 °C with a heating rate of 10 °C min$^{-1}$, under nitrogen atmosphere.

2.2. Synthesis and Crystallization of H$_2$Br$_4$tp·2MeCN ($1_{\text{MeCN}}$)

A mixture of H$_2$Br$_4$tp (5 mg) and MeCN (2 ml) was added into a 25 mL Teflon-lined reactor, sealed in a stainless-steel autoclave, and placed in an oven. The mixture was heated from room temperature to 110 °C under autogenous pressure for 1 h and then cooled down to room temperature. Colorless block-shaped crystals of $1_{\text{MeCN}}$ were obtained. Anal. calc. for C$_{12}$H$_8$Br$_4$N$_2$O$_4$: C, 25.56%; H, 1.43%; N, 4.97%. Found: C, 25.60; H, 1.43; N, 4.82%. FT-IR (ATR, ν/cm$^{-1}$, s for strong, m medium, w weak): 3514w, 3421w, 3149w, 1571s, 1415s, 1324s, 1570s, 1182w, 1069m, 919w.

2.3. Synthesis and Crystallization of H$_2$Br$_4$tp·2MeOH ($2_{\text{MeOH}}$)

Colorless block-shaped crystals of $2_{\text{MeOH}}$ were synthesized by a similar procedure as $1_{\text{MeCN}}$ above except that MeCN was replaced with MeOH. Anal. calc. for C$_{10}$H$_{10}$Br$_4$O$_6$: C, 22.01; H, 1.85%. Found: C, 22.26; H, 1.91%. FT-IR (ATR, ν/cm$^{-1}$): 3514w, 3421w, 3149w, 1571s, 1415s, 1324s, 1570s, 1182w, 1069m, 919w.
2.4. X-ray Crystallography

Suitable crystals of 1MeCN and 2MeOH were carefully selected and mounted on MiTeGen micromounts using paratone-N oil. X-ray diffraction data were collected using a Bruker D8 QUEST CMOS PHOTON II with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 296(2) K. Data reduction was performed using SAINT, and the SADABS scaling algorithm [18] was used for absorption correction. The structure was solved with the ShelXT structure solution program using combined Patterson and dual-space recycling methods [19]. The structure was refined by least squares using ShelXL [20]. All non-H atoms were refined anisotropically. The H atoms of solvent molecules were positioned geometrically with C–H = 0.96 Å and refined using a riding model (AFIX137 for methyl H atom in ShelXL program) with fixed displacement parameters Uiso(H) = 1.5 Ueq(C). The O–H hydrogen atoms were located on difference Fourier maps but refined with O–H = 0.82 ± 0.01 Å with Uiso(H) = 1.5 Ueq(O). A summary of crystal data and structural refinement parameters for 1MeCN and 2MeOH is given in Table 1.

Table 1. Crystal data and structure refinement for 1MeCN and 2MeOH.

| Compound | H2Br4tp 2MeCN (1MeCN) | H2Br4tp 2MeOH (2MeOH) |
|----------|------------------------|------------------------|
| Empirical formula | C12H16Br4N2O4 | C10H18Br4O6 |
| Formula weight | 563.84 | 545.82 |
| Temperature (K) | 296(2) | 296(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | P21/c |
| a (Å) | 6.1577(6) | 11.8461(11) |
| b (Å) | 8.3463(8) | 9.2213(8) |
| c (Å) | 9.2327(9) | 15.1000(14) |
| α (°) | 68.241(3) | 90 |
| β (°) | 78.863(4) | 107.840(3) |
| γ (°) | 84.436(4) | 90 |
| V (Å³) | 432.23(7) | 1570.2(2) |
| Z | 1 | 4 |
| ρcalc (g/cm³) | 2.166 | 2.309 |
| μ (mm⁻¹) | 9.327 | 10.271 |
| F(000) | 266 | 1032 |
| θ range (°) | 3.4–32.1 | 2.8–32.1 |
| Reflections collected | 17952 | 50246 |
| Independent reflections | 3149 | 5490 |
| Rint, Rsigma | 0.0566, 0.0429 | 0.0968, 0.0650 |
| Data/restraints/parameters | 3149/1/106 | 5490/4/200 |
| Goodness-of-fit on F² | 1.028 | 1.025 |
| R1, wR2 [I > 2σ(I)] | 0.0427, 0.0731 | 0.0519, 0.0944 |
| R1, wR2 [all data] | 0.0909, 0.0871 | 0.1189, 0.1167 |
| Δρmax, Δρmin (e Å⁻³) | 0.57, −0.69 | 0.93, −1.14 |
| CCDC number | 2005667 | 2005668 |

3. Results and Discussion

3.1. Structural Description

Colorless block-shaped crystals of 1MeCN and 2MeOH were obtained upon the crystallization of H2Br4tp from the solvents MeCN and MeOH at 110 °C for 1 h in a 25 mL Teflon-lined stainless-steel container. Alternatively, single crystals of these two solvates can also easily be grown by dissolving H2Br4tp in each respective solvent and by allowing them to crystallize by slow evaporation at room temperature for 24 h. The single-crystal X-ray diffraction analysis revealed that the solvates crystallize in the centrosymmetric system with space groups P-1 and P21/c for 1MeCN and 2MeOH, respectively. These solvates have a similar 1:2 stoichiometric ratio of H2Br4tp and solvent molecules. Figure 1 shows the molecular structure with the atomic numbering schemes of the solvates. The asymmetric
unit of $1_{\text{MeCN}}$ contains half a molecule of H$_2$Br$_4$tp located at a center of inversion and one MeCN molecule. In contrast, there are one H$_2$Br$_4$tp molecule and two MeOH molecules in the asymmetric unit of $2_{\text{MeOH}}$.

In the crystal of $1_{\text{MeCN}}$, the H$_2$Br$_4$tp molecules are linked by Br···O halogen bond and weak van der Waals (vdW) O···O interactions to generate a two-dimensional (2D) sheet structure along the a axis (Figure 2a). The observed Br···O halogen bonding interaction (3.270(3) Å) between bromine atom and the oxygen carbonyl atom in $1_{\text{MeCN}}$ is ≈3% shorter than the sum of the vdW radii of the Br and O atoms (3.37 Å) [21], and the C–Br···O bond angle (155.3°) is slightly bent. In contrast, the non-bonded O···O distance (3.038(6) Å) between the oxygen atoms of the carboxyl groups is almost the same as the sum of the vdW radii of the two oxygen atoms (3.04 Å). Apparently, the solvent MeCN molecules are located between the 2D layered sheets and participate in O–H···N and C–H···O hydrogen bonding interactions (Table S1) in the tetrameric motif with graph set notation $R^4_4$(16) [22] (Figure 2b). Such interactions along with additional weak type I Br···Br halogen bonds and Br···C contacts (Br···C ≈3.5 Å) [23] link the 2D sheets into a 3D supramolecular architecture. Further investigation of the packing structure found that the centroid–centroid distances between the stacked C=N group of the MeCN molecule and the aromatic ring of the H$_2$Br$_4$tp molecule is 3.997(5) Å, which indicates a weak $\pi$···$\pi$ interaction [24]. This also contributes to the packing stabilization of the solvate $1_{\text{MeCN}}$. The geometric parameters for the halogen bonds and the hydrogen bonds of the solvates are provided in Table 2 and Table S1 (Supplementary Materials), respectively.

For $2_{\text{MeOH}}$, the H$_2$Br$_4$tp molecules are assembled together by Br···O halogen bonding (3.043(3) and 3.087(3) Å) and O···O (3.022(3) Å) interactions similar to that of $1_{\text{MeCN}}$ above, giving rise to a 2D sheet structure approximately along the a axis, as illustrated in Figure 3a. However, unlike $1_{\text{MeCN}}$, several Br···Br interactions (3.7233(7)–3.8871(8) Å) of types I and II exist in the crystal structure of $2_{\text{MeOH}}$ (Figure 3b), and these values are slightly longer than the sum of the vdW radii, indicative of weak interactions. It should also be noted that the Br···O distances in $2_{\text{MeOH}}$ (Table 2) are much shorter than those observed for $1_{\text{MeCN}}$. This is possibly due to the influence of the geometry of the MeOH molecules on packing. H$_2$Br$_4$tp and the MeOH molecules can behave as either hydrogen bond donor or acceptor sites similar to that of $1_{\text{MeCN}}$ and interact with each other via the O–H···O and C–H···O hydrogen bonding interactions (Table S1), leading to the formation of the
tetrameric hydrogen bonding motif with an $R_4^4(12)$ graph set (Figure 3c). These interactions serve to connect the sheets into a 3D architecture.

Table 2. Parameters of the $C\rightarrow Br\rightarrow X$ halogen bonds for $1_{\text{MeCN}}$ and $2_{\text{MeOH}}$.

|          | d($Br\rightarrow X$) (Å) | $\angle (C\rightarrow Br\rightarrow X)$ (°) | Symmetry Code         |
|----------|--------------------------|---------------------------------------------|-----------------------|
| $1_{\text{MeCN}}$ |                          |                                             |                       |
| C3–Br1…Br2 | 3.9434(7)                | 85.26(10)                                   | $-x, -y, 1 - z$       |
| C4–Br2…O2 | 3.270(3)                 | 155.24(11)                                  | $x, y, z - 1$         |
| $2_{\text{MeOH}}$ |                        |                                             |                       |
| C3–Br1…O4 | 3.087(4)                 | 173.41(14)                                  | $1 - x, 1/2 + y, 3/2 - z$ |
| C4–Br2…O1 | 3.043(3)                 | 177.69(15)                                  | $1 - x, 1/2 + y, 3/2 - z$ |
| C4–Br2…Br3 | 3.7233(7)                | 89.77(13)                                   | $x, 1/2 - y, z + 1/2$ |
| C4–Br2…Br4 | 3.8507(8)                | 119.49(13)                                  | $x, 1/2 - y, z + 1/2$ |
| C8–Br3…Br1 | 3.7989(7)                | 176.35(13)                                  | $x, 1/2 - y, z - 1/2$ |
| C8–Br3…Br3 | 3.7994(11)               | 77.52(13)                                   | $1 - x, -y, 1 - z$   |
| C8–Br3…Br4 | 3.8871(8)                | 103.15(13)                                  | $1 - x, -y, 1 - z$   |

Figure 2. Partial views of (a) the 2D sheet constructed by halogen bond $Br\rightarrow O$ and vdW $O\rightarrow O$ interactions (dashed lines) between the $H_2Br_4tp$ molecules and (b) the 1D chain formed by $O-H\rightarrow N$ and $C-H\rightarrow O$ interactions (dashed lines) with an $R_4^4(16)$ graph set existing between the $H_2Br_4tp$ and the MeCN molecules in $1_{\text{MeCN}}$. 
hydrogen bonding interactions (Table S1), leading to the formation of the tetrameric hydrogen bonding motif with an $R_{44}(12)$ graph set (Figure 3c). These interactions serve to connect the sheets into a 3D architecture.

Figure 3. Partial views of (a) the 2D sheet constructed by Br···O and O···O interactions (dashed lines) between the H$_2$Br$_4$tp molecules, (b) the Br···Br interactions of types I and II, and (c) the 1D chain formed by O···H···O and C···H···O interactions (dashed lines) with an $R_{44}(12)$ graph set existing between the H$_2$Br$_4$tp and the MeOH molecules in 2MeOH.

Figure 4 depicts the packing diagrams and the contact surface of the channels viewed along the $a$ and $b$ axes for 1MeCN and 2MeOH, respectively. Although both solvates have the same composition and stoichiometry, it can clearly be seen that different solvents lead to differences in molecular orientation within the crystal packing. This can be attributed to the nature (size, shape, and intermolecular interaction capabilities) and the different
roles of solvent molecules during supramolecular framework assembly. It appears that the space accommodating the MeCN molecule in 1MeCN has a cylinder-like geometry (1D channel along the a axis) with discontinuous voids (Figure 4a). For 2MeOH, the space occupied by the MeOH molecules shows continuous in-void volume maps (Figure 4b) that propagate in two directions (the ac plane). Despite the different packing arrangements, either solvent MeCN or MeOH molecules are involved in the hydrogen bonding with similar tetrameric hydrogen-bonding motifs as described above. A comparison of the packing efficiency (Ck) using PLATON [25] revealed that 1MeCN (Ck = 46.9%) possesses a lower packing efficiency than that of 2MeOH (Ck = 52.1%). This result demonstrates that the components in the solvate 2MeOH pack more tightly, which may be attributed to the presence of numerous Br···O, Br···Br, and Br···π halogen bonding and classical O–H···O hydrogen bonding interactions. Furthermore, the potential solvent-accessible void space after the removal of solvent molecules, also calculated using PLATON, was estimated to be ≈34.8% and 30.4% for 1MeCN and 2MeOH, respectively. In this regard, the 2D supramolecular frameworks with visualized surfaces of void structures of these solvates may potentially serve as a stable soft host framework for polar organic molecules.

![Figure 4](image_url)

**Figure 4.** Partial views of crystal packing with solvent molecules displayed using the space-filling model and the contact surface of the cavities calculated in mercury using a probe radius of 1.2 for (a) 1MeCN and (b) 2MeOH.

Additionally, given the abundance of bromine atoms in the H2Br4tp molecular tectons, perhaps it is not surprising that Br···O, Br···Br, and Br···π synthons were the most frequently found halogen bonding motifs in 1MeCN and 2MeOH. Our previous studies also indicated that this type of interaction was common in H2Br4tp solvates with acetone, ethanol, dimethyl sulfoxide, and ethylene glycol solvents [23] and is mainly responsible for the formation of their layered sheets. Despite this, each solvate exhibits subtle differences in overall packing due to different hydrogen bonding and the orientation of the solvent molecules. Notably, H2Br4tp can selectively accommodate MeOH molecules relative to other solvents. This is probably related to the molecular shape and size, the acidity scale, as well as some specific intermolecular interactions.
3.2. Hirshfeld Surface Analysis

The nature of the intermolecular interactions between the molecules within the crystal structure of the solvates 1MeCN and 2MeOH was further quantified and visualized by Hirshfeld surfaces [26] and their associated 2D fingerprint plots [27] performed with CrystalExplorer [28]. The shorter and longer contacts on the Hirshfeld surfaces are indicated as red and blue spots, respectively, while white spots indicate contacts with distances approximately equal to the sum of the vdW radii. The function $d_{\text{norm}}$ (normalized distance) is a ratio enclosing the distances of any surface point to the nearest interior ($d_i$) and exterior ($d_e$) atom and the vdW radii of the atoms. As can be seen from the structural analysis above, the bromine atoms of the host H2Br4tp molecules are involved in Br⋯Br, Br⋯O, and Br⋯π halogen bonding interactions. The contributions of such interatomic contacts to the $d_{\text{norm}}$ surface in these solvates are compared and shown in Figure 5.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Two-dimensional fingerprint plots of (a) 1MeCN and (b) 2MeOH, showing all interactions, and those delineated into intermolecular contacts involving bromine atoms.
It is evident that the 2D fingerprint plots of all contacts among these solvates differ significantly due to the differences in packing arrangements and intermolecular interactions in the solid state. Specifically, there is major significant difference in the Br···Br contact, which comprises 4.4% and 12.1% of the $d_{\text{norm}}$ surface for 1MeCN and 2MeOH, respectively, while the Br···O contacts show quite similar contributions to the surface (9.3% for 1MeCN and 8.5% for 2MeOH). Apparently, both solvates feature Br···C/C···Br contacts (9.9% for 1MeCN and 10.8% for 2MeOH), which are manifested as weak Br···π contacts. The Br···H/H···Br contacts also have a significant contribution towards the crystal stabilization of these solvates (22.3% for 1MeCN and 20.3% for 2MeOH). It should be noted that O···O contacts for these solvates contribute a negligible percentages (1.8% for 1MeCN and 1.1% for 2MeOH) towards the total surface area. Furthermore, the dominant interactions between H and O or N atoms, corresponding to the discussed hydrogen bonding interactions have also been visualized by selecting the host H2Br4tp molecules as the object. As can be clearly seen from Figure 6, these solvates exhibit red spots on the $d_{\text{norm}}$ surface, signifying close contacts, which originate from O–H···O or O–H···N interactions, comprising 5.0% and 20.4% of the total surface area for 1MeCN and 2MeOH, respectively. It is of interest to note that the contributions to the $d_{\text{norm}}$ surface due to H···H contacts are 5.7% in 1MeCN and 18.5% in 2MeOH, implying vDW interactions being dominant for the supramolecular organization in 2MeOH. In addition, the small contributions of the other weak intermolecular C···C (3.2% for 1MeCN and 1.6% for 2MeOH), C···H/H···C (3.9% for 1MeCN and 0.4% for 2MeOH), C···O/O···C (3.8% 2MeOH), and H···N/N···H (8.3% for 1MeCN) contacts have negligible effects on the packing (Figure 7).

![Figure 6](image-url) Illustration of the Hirschfeld surfaces mapped with $d_{\text{norm}}$ for the intermolecular hydrogen bonding interactions between H2Br4tp and solvent molecules for (a) 1MeCN and (b) 2MeOH.

![Figure 7](image-url) Quantitative results of different intermolecular contacts contributing to the Hirschfeld surfaces of the solvates.
3.3. Thermal Analysis and Structural Transformation

To evaluate the thermal behaviors of the solvates of H₂Br₄tp, TGA was performed on crystalline samples in the temperature range of 30 to 500 °C under nitrogen atmosphere. The TGA profiles of 1MeCN, 2MeOH, and H₂Br₄tp are compared in Figure 8a. It was found that no weight loss was observed before 280 °C in the TGA curve of H₂Br₄tp, suggesting the absence of solvent molecules in its crystal structure. Meanwhile, the TGA curves of 1MeCN and 2MeOH show that the solvent (MeCN or MeOH) molecules are gradually lost from room temperature to ~80–95 °C, and then decomposition is observed beyond ~250 °C.

According to the TGA profiles, it is interesting that the structures of the host molecules remained intact after desolvation. Notably, PXRD patterns of the desolvated samples in Figure 8b,c also clearly reveal the formation of a new phase-pure material, in which the peak positions correspond well with H₂Br₄tp in the monoclinic C2/m space group [17]. Furthermore, the recyclability of the solvent release and resorption experiments was also examined. The crystalline samples of each solvate (~10 mg) were placed in a crucible (≈10 mbar pressure) for 1 h. Indeed, the solvate form changes to the unsolvated phase, which can be confirmed by the disappearance of PXRD peaks at 2θ = 10.40 and 11.35° for 1MeCN and at 2θ = 7.83° for 2MeOH. Additionally, the absence of the solvent molecules was also evidenced by the disappearance of the C≡N stretching vibration band of a nitrile group of MeCN (νC≡N = 2218 cm⁻¹) in the IR spectrum of 1MeCN (Figure 8d) while only negligible changes could be observed in the IR spectrum of 2MeOH. Both of the desolvated samples could be recovered to their original phase upon resolvation with the corresponding solvent (MeCN or MeOH) and heating (110 °C, 1 h) in a Teflon-lined stainless autoclave. Alternatively, crystals of the original...
phase can be obtained by simply immersing the desolvated samples in MeCN and MeOH solutions for 24 h. This reversible behavior can be repeated a number of times, which was confirmed by PXRD and IR spectroscopic techniques.

For a better understanding of the dynamic structural phase transition, detailed crystal structural information as well as intermolecular interactions of the desolvated crystals are very important. Although the desolvated crystals were found to possess similar morphologies to those of the original solvate forms and maintained their crystallinity, as confirmed by the PXRD experiments, they were found to diffract very poorly even at a medium resolution shell. Thus, single crystal structure determinations of these desolvated forms in this work were not possible. Despite several recrystallization attempts, regrettably, all failed to yield crystals of H₂Br₄tp alone. Fortunately, the solid-state structure of H₂Br₄tp determined from PXRD data was reported by Kumar et al. [17]. In packing, intermolecular O–H···Br hydrogen bonds are mainly responsible for the formation of a 2D sheet. Based on this evidence as well as our findings, we note that halogen bonding can be cooperative or competitive with hydrogen bonding during the desolvation–resolvation process.

4. Conclusions

In summary, H₂Br₄tp, a bromine and carboxyl-containing molecule, showed significant potential as a building block in the assembly of a 2D halogen-bonded sheet in crystalline state through a range of different halogen bonding synthons. These 2D assemblies can form 1:2 cocrystal solvates with MeCN and MeOH, in which the formation relies on very similar hydrogen bonding motifs between the respective components. Each solvate crystal showed distinct packing arrangements, which result from permutations of different halogen bonds. PXRD analysis and IR spectroscopy showed that the structural phase transitions between the solvated and the unsolvated crystals are reversible upon the release/resorption of solvent molecules. This study assessed the importance of the cooperative effect of halogen bonding in combination with hydrogen bonding interactions for engineering solvate crystals, permitting reversible release and resorption of solvent molecules.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4352/11/2/198/s1. Table S1: Hydrogen bond geometry (Å, ′) for 1MeCN and 2MeOH.

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