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Isostructurality in the Guest Free Forms and in the Clathrates of 1,3,5-Triethyl-2,4,6-tris(4-halophenoxy)methylbenzenes

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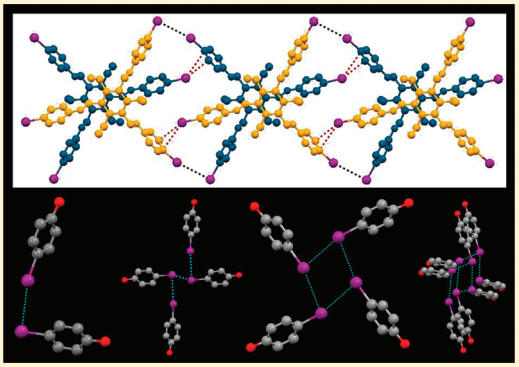
Supporting Information

ABSTRACT: Crystal structures of the guest free forms and some solvates of 1,3,5-triethyl-2,4,6-tris(4-halophenoxy)methylbenzenes (1X, X = I, Br, Cl, F) have been studied. The guest free forms of 1I, 1Br, and 1Cl are isostructural, but the crystal structure of 1F is different from the heavier halogen analogues. An entirely different crystal structure of the Me analogue, which is known to be isosteric to the corresponding bromo compound, shows the importance of the electronic factors of the halogens in this series of structures. 1I and 1Br form four types of architectures in their solvates depending upon the inter-halogen interaction geometries. All these solvates are two dimensionally isostructural to the guest free form. 1Cl forms three different types of frameworks in its solvates, and the ethylacetate solvates of the 1I, 1Br, and 1Cl are isostructural. 1F forms only one type of solvate which is isostructural to the corresponding 1Cl solvate.



INTRODUCTION

Halogen bonding[1] is a class of weak noncovalent interactions that occurs in a system as A−Hal···B, when a halogen atom approaches a Lewis base B possessing a lone pair. The most interesting aspect of the halogen bonding is that it is an interaction between two electronegative atoms that is expected to be repulsive but is in fact attractive in nature. Statistical reports suggest that the halogen atoms, especially the heavier ones, show a strong anisotropic shape in their electron cloud owing to their polarization.[2] The interaction energy of such systems spans over a wide range, 10−200 kJ mol^{-1}.[3] In general, halogens are thought to polarize in a manner that they are electron deficient along the bond axis and electron rich in the perpendicular direction to it. Thus, the approach of any system with suitable complementarity along these vectors would result in a stable interaction. The above facts suggest that so-called halogen bonds, owing to their strong directionality and strength, can be used as a tool for promoting specific crystal packing motifs and thus could be a handy tool in crystal engineering.[4] In particular, the inter-halogen interactions too have a directional feature which has been generalized by Desiraju and Parthasarathi.[5] According to them, halogen···halogen interactions are seen to be having two preferred geometries, Type-I ($\theta_1 \cong \theta_2$) and Type-II ($\theta_1 \cong 180°$, $\theta_2 \cong 90°$). The type-I contact is merely a result of van der Waals contact, whereas the type-II contact is a function of electrostatic forces resulting from the polarization and anisotropy associated with the electron cloud of the halogen. Recently, Guru Row and co-workers have categorized type-I inter-halogen interaction into two subgroups, cis and trans.[6] As far as the electron acceptance by a halogen is concerned, the tendency increases down the Group 17 in the periodic table as F < Cl < B < I.[7] This behavior could be attributed to the higher polarizability of I compared to F. Although theoretically F could be a good acceptor, because of its small size, poor polarizability, and high electronegativity, involvement of fluorine has been a matter of debate over the years. Recently, Guru Row and co-workers have reported a quantitative analysis of Cl···F and F···F interactions in their work with 2-chloro-4-fluorobenzoic acid and 4-fluorobenzamide.[8] Investigations are also reported in the literature regarding the preferential occurrence of halogen bonding over hydrogen bonding in systems containing both kinds of functional groups.[9]

Systems exhibiting halogen bonding have been designed that show a wide range of applications. Nangia and co-workers have reported a library of halogen substituted 2-halo-3-hydroxypyridine, 2-halo-3-hydroxypyridine *N*-oxides, and 2-halo-3-aminopyridine where the inter-halogen interactions have been used as a tool to promote crystallization of the compounds in noncentrosymmetric space groups, producing models for studying nonlinear optical (NLO) properties.[10a] Earlier, Thalladi et al. reported a family of isotropic halogen containing 2,4,6-triaryloxy-1,3,5-triazines as candidates for NLO studies.[10b] By making use of the robust C−I···N interactions, Metrangolo et

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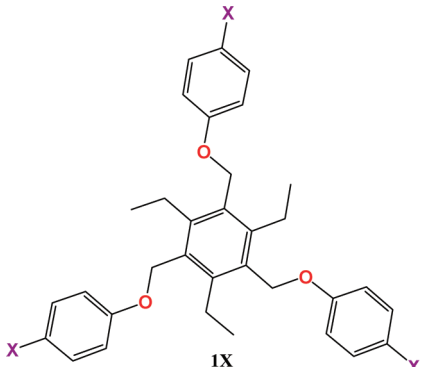
al. have designed poly(propylenimine) based dendrimers via cocrystallization with bipyridine homologues.[10c] In an earlier report, Resnati and co-workers investigated the possibility and the potency of the halogen···N interaction in various organic systems.[10d] Xu et al. used the halogen bonding as a steering force in the synthesis of a new class of liquid crystalline supramolecular polymers.[10e] Halogen bonds have also been combined with hydrogen bonds in the engineering of desired network structures.[11]

Isostructurality is the phenomenon in which two different systems show similar kinds of structures.[12] Study on isostructurality opens up avenues for the study of periodicity in chemical or physical properties of similar systems. There are several reports where exchange of functional groups do not alter the packing in a crystal structure.[13] Halogen groups are prone to show such behavior more frequently than all other functional groups. Me/Cl and Me/Br exchange are also well-known to produce isostructurality.[14]

Herein we report the crystal structures of the guest free forms and some solvates of 1,3,5-triethyl-2,4,6-tris(4-halophenoxy)methylbenzenes. We also have studied the Me analogue of the compound to understand the importance of the electronic factors of the halogens (Scheme 1).

Scheme 1. The 1,3,5-Triethyl-2,4,6-tris(4-halophenoxy)methylbenzene (1X, X = I, Br, Cl, F, Me) Employed for the Study



1X
X = I, Br, Cl, F, Me

RESULTS AND DISCUSSION

In this series of 43 crystal structures, there are six different types of host architectures in the host–guest systems (HG1–6), and three different types of structures in the guest free forms (GF1–3) have been observed (Table 1). Among the six host architectures, four forms (HG1–4) were obtained in the 1I solvates, and two new forms (HG5 and 6) were obtained in the 1Cl solvates. The form HG2 is also present among the 1Cl solvates. The 1Br and 1F solvates are isostructural to the 1I and 1Cl solvates, respectively. The guest free forms of 1I, 1Br, and 1Cl are isostructural (GF1), but the crystal structures of 1F (GF2) and 1Me (GF3) are different from the heavier halogen derivatives.

Guest Free Forms. The guest free form (type GF1, Figure 1a) of the 1I compound was obtained from an acetonitrile solution of the compound which was solved in a monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The molecule is highly flexible in nature. Two of the phenoxy groups are oriented above the plane of the middle aromatic ring, and the third phenoxy group is oriented down the ring.

Table 1. List of the Network Systems of the Halogenated Compounds Crystallized from Different Solvents

Sl. no.	solvents	1I	1Br	1Cl	1F
1	acetonitrile	GF1	GF1	GF1	GF2
2	benzene	HG1	HG1	NSC[a]	NSC
3	pyridine	HG1	HG3	GF1	GF2
4	toluene	HG2	HG2	HG5[c]	HG5
5	*p*-xylene	HG2	HG2	HG5	HG5
6	*m*-xylene	HG2	HG2	HG5	HG5
7	*o*-xylene	HG2	HG1	HG5[c]	HG5
8	mesitylene	HG2[b]	HG2[b]	NSC	NSC
9	ethylacetate	HG2[b]	HG2[b]	HG2[b]	GF2
10	chloroform	HG3	HG3	GF1	NSC
11	1,2-dibromoethane (DBE)	HG3	NSC	GF1	NSC
12	1,2-dichloromoethane (DCE)	HG3	NSC	NSC	NSC
13	dioxane	HG3	HG3	HG6	NSC
14	tetrachloromethane (TCM)	HG3	HG3	NSC	NSC
15	tetrahydrofuran (THF)	HG3	HG3	NSC	NSC
16	picoline	HG4	HG4	GF1	GF2

[a]NSC: No single crystal obtained for X-ray diffraction. [b]Squeezed. [c]Partially squeezed.

One ethyl group of the molecule is disordered over two positions. Halogen bonds play an important role in this crystal structure. The crystal packing is guided by a type-II I···I interaction involving two of the three halogens of a molecule and a I···π halogen bond involving the third halogen to form a one-dimensional (1-D) molecular tape running parallel to the [110] direction (Figure 1b). The molecules also pair up in the tape to form a Piedfort unit with small stacking offset. Diffraction quality single crystals of the 1Br and 1Cl compounds were obtained from the acetonitrile and chloroform solutions respectively. Even though the bromo (1Br) and the chloro (1Cl) analogues are isostructural to the 1I crystal structure (GF1), they crystallize in the $P2_1/c$ space group with two and three molecules in the asymmetric units, respectively. In the crystal structure of 1Br, all the three phenoxy groups in one molecule are directed above the plane of the middle ring, whereas in the other molecule, the arrangement of the phenoxy groups is similar to the 1I molecule. On the other hand, in the case of the 1Cl crystal structure, the conformations of the two molecules are similar to the former 1Br molecule and the third one is similar to the latter 1Br molecule. Hence, this is a case of conformational isomorphism, the occurrence of different conformers in the same crystal structure.[15] Interestingly, 1I, 1Br, and 1Cl are isostructural in spite of different molecular conformations, and the Z′ value also increases gradually from 1 to 3. This could be attributed to the increasing mosaicity in the crystal structures from 1I to 1Cl. This fact suggests that this type of crystal packing pattern (type GF1) could be more suitable for the heavier halogen derivatives and beyond chlorine this packing motif is not sustained. As a result, the crystal structure of 1F (GF2) is different from these three analogues (Figure 1c). The guest free form of 1F crystallizes from an ethylacetate solution in a monoclinic space group $P2_1/n$ and a single molecule is present in the symmetry independent unit. The intermolecular interactions in this type of structure (GF2) are not so interesting. The F groups are involved in the weak C–H···F interactions and the molecules also form Piedfort units with a small offset in this crystal structure. The methyl group is known to be isosteric to Br. Our calculation by the

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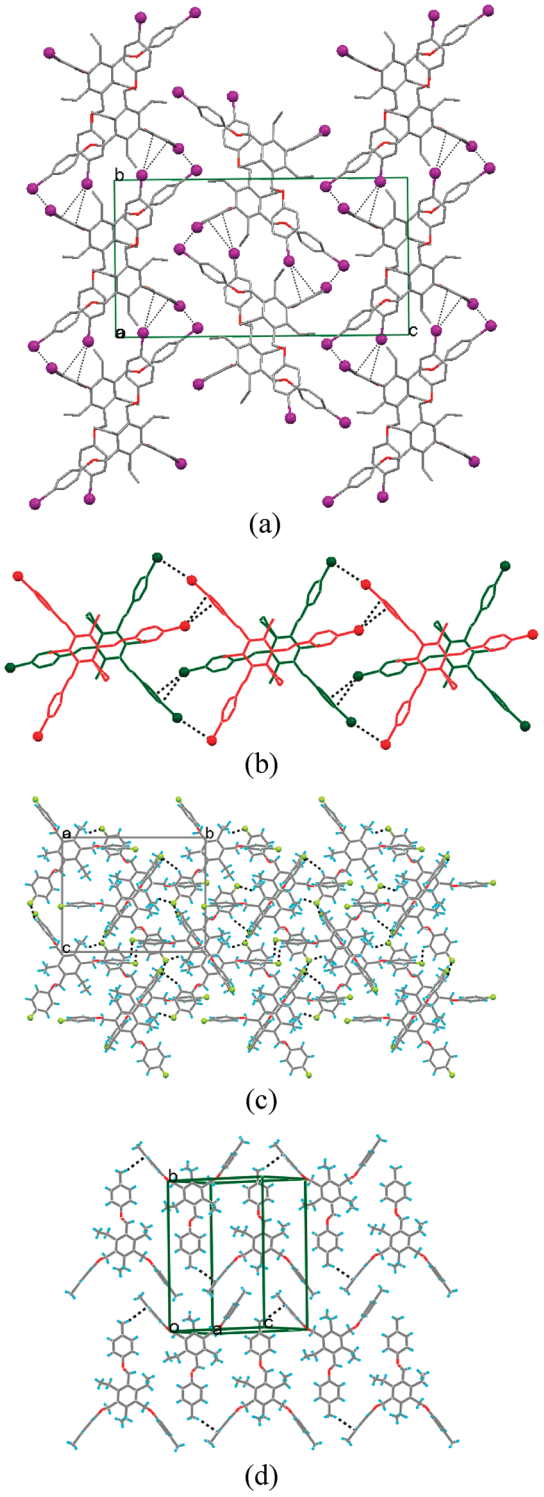

Figure 1. Crystal packing in the guest free forms: (a) molecular packing diagram in the crystal structure of 1I, (b) I···I, I···π halogen bonds, and Piedfort unit directed molecular tape in 1I (GF1). (c) Weak C−H···F hydrogen bond directed crystal packing in 1F (GF2). (d) Packing of the 1Me molecules in a two-dimensional layer (GF3).

SPARTAN'10 (AM1) program shows that the volumes of the I, Br, Cl, F, and Me groups are 32.0, 25.7, 21.1, 12.7, and 26.0 Å^3, respectively (volume of X = PhX−0.5(biphenyl); the dihedral angle of the phenyl rings has been taken as 90° to avoid *o*-hydrogen interactions). To understand the importance of the electronic factor of the halogens, we have studied the crystal structure of 1Me to compare with the halogenated compounds. Diffraction quality single crystals of 1Me were obtained from a dimethylformamide solution of the compound, and the system crystallizes in the $P2_1/n$ space group with one molecule in the asymmetric unit. The crystal packing of 1Me (GF3) is entirely different (Figure 1d) from the halogenated compounds (GF1 or 2), which suggests that interaction of the halogens plays an important role in determining the self-assembly process of the molecules in the crystal structures (GF1 and 2). Nangia and co-workers have reported similar phenomena, where the halogenated compounds formed a series of clathrate structures guided by inter-halogen interactions,[13a,16a] but the corresponding methyl derivative formed a close packed structure.[16b]

Solvates of 1I and 1Br. The solvates of 1X were obtained by slow evaporation of the solvents from the solution of 1X in the corresponding solvents at room temperature. There are four different types of host networks (HG1−4) observed in the 1I and 1Br clathrates. Except the picoline solvates, which crystallize in $P2_1/n$ space group, all the other three types of systems crystallize in the $P\bar{1}$ space group with one molecule each of the host and the guest species in the asymmetric unit. In all these crystal structures, two halogens are involved in a type II inter-halogen interaction and the third halogen is involved in a halogen···π interaction. The crystal structures of the pyridine and benzene solvates of 1I (1I·pyridine, 1I·benzene) and the benzene and *o*-xylene solvates of 1Br (1Br·benzene, 1Br·*o*-xylene) belong to the HG1 network type. Similar to the guest free form, the host networks are guided by a type II halogen dimer interaction and a halogen···π interaction. In the case with the pyridine solvate, the system is further stabilized by a N···I halogen bonds between the host and the guest molecules (Figure 2a). Except the 1Br·*o*-xylene solvate, the ethylacetate, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene solvates of 1I and 1Br form a HG2 type of host network. In these structures, the halogen···π interaction remains intact, but the halogens form a "Z" shape halogen tetramer (Figure 2b). We could not grow diffraction quality single crystals of 1Br from 1,2-dibromoethane (DBE) and 1,2-dichloroethane (DCE), except these two solvates of 1Br, the chloroform, tetrachloromethane (TCM), DBE, DCE, dioxane, and tetrahydrofuran (THF) solvates of 1I and 1Br along with the 1Br·pyridine solvate adopt a HG3 type architecture. In these structures, along with the halogen···π interaction, the halogens are also involved in the formation of a cyclic halogen tetramer synthon (Figure 2c). The interesting part in this type of system is that the 1Br·pyridine does not adopt the structure of 1I·pyridine, where the pyridine molecule forms a halogen bond to the iodo group. This fact supports the idea that an iodo group is a better candidate for halogen bonding over a bromo group. The picoline solvates of 1I and 1Br are isostructural (HG4) and crystallize in the monoclinic space group $P2_1/n$ with one molecule, each of the host and the guest species in the asymmetric unit. Two of the halogens of a molecule are involved in forming infinite helical chains with opposite handedness, running parallel to the crystallographic *b* axis, via type II inter-halogen interactions. Also in this structure the third halogen is involved in a halogen···π interaction (Figure 2d,e). The guest molecules are hydrogen bonded via C−H···N interactions to form a molecular chain, running through the channel, generated in the host network, parallel to the *b* axis.

Solvates of 1Cl and 1F. The ethylacetate solvate of 1Cl (1Cl·EtOAc) is isostructural to the HG1 framework and crystallizes in the space group $P\bar{1}$ with a host to guest ratio of

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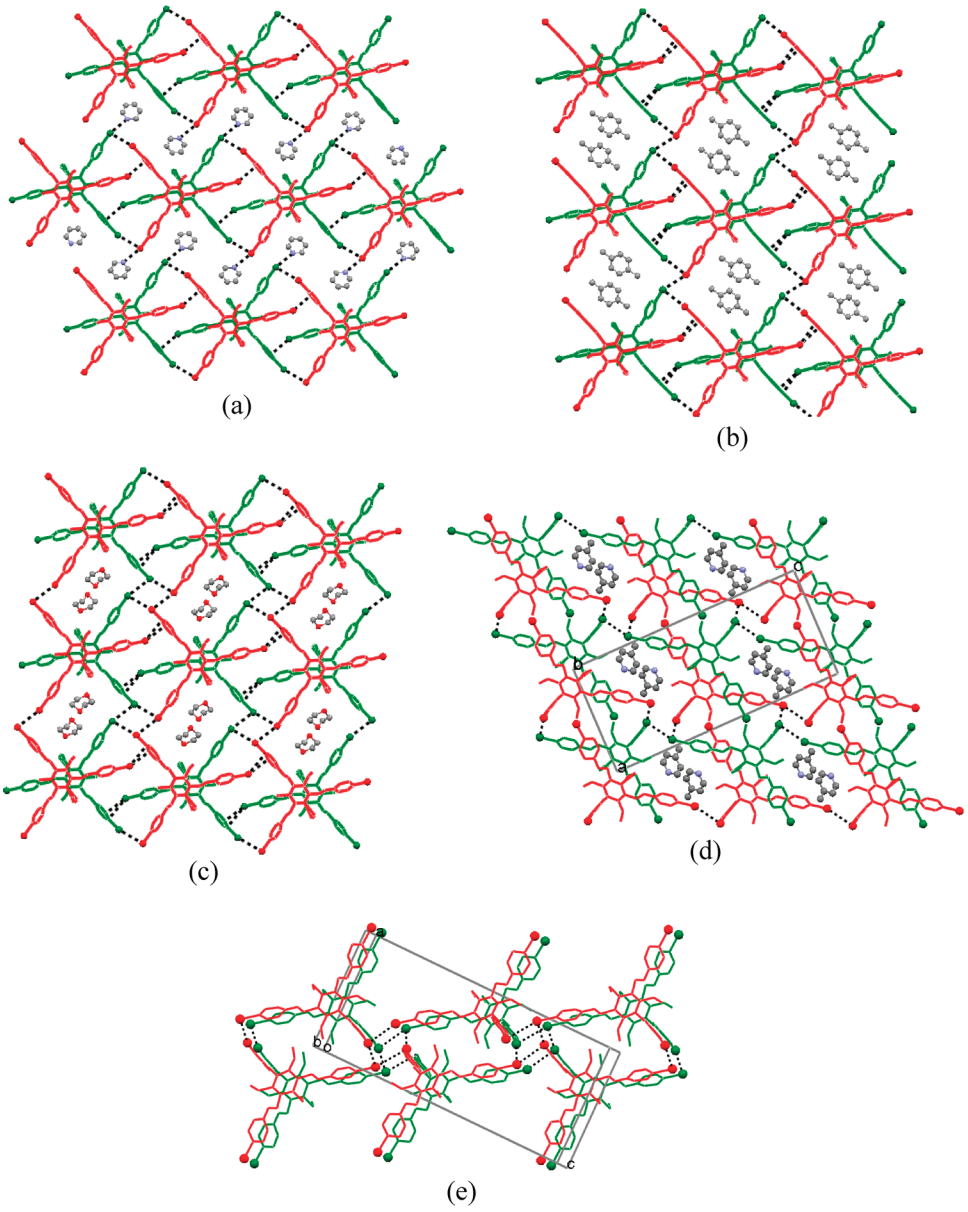

Figure 2. (a) I···I dimer and I···π halogen bonds directed HG1 type of open framework in 1I·pyridine. Pyridine molecules are connected to the host molecules via I···N halogen bonds. (b) 1I molecules are assembled via "Z" shape iodo tetramer and I···π halogen bonds in the HG2 type of network in 1I·*p*-xylene. (c) HG3 type of network formed by the 1I host molecules via cyclic iodo tetramer and I···π halogen bonds in 1I·dioxane system. (d) Helical arrangement of the 1I host molecules via helical I···I interactions and I···π halogen bonds in the type HG4, 1I·picoline system. (e) The 1D infinite right and left handed helices of type II I···I interactions along the *b* axis.

1:1. But the toluene, *o*-xylene, *m*-xylene, *p*-xylene, and the dioxane solvates of 1Cl form different types of networks. The first four solvates of 1Cl and 1F are isostructural (HG5) and crystallize in the space group $P\bar{1}$. The host to guest ratio is found to be 1:2 in these systems. In this type of structure, the halogens are involved only in the weak C−H···halogen type of hydrogen bonds (Figure 3a) to form a square grid kind of network where the guest molecules are incorporated inside the cavities. The dioxane solvate of 1Cl (1Cl·dioxane) forms an interesting framework (HG6) in this series. The system crystallizes in a monoclinic space group $P2_1/n$ with one molecule of the host and a half molecule of the guest moieties in the asymmetric unit. A molecular tape is formed via Cl···Cl type-II interactions and Piedfort units. The guest molecules occupy the cavities, generated within the tape, and are hydrogen bonded with the host network via weak C−H···O and C−H···Cl interactions (Figure 3b). Interestingly, this structure has close resemblance to the guest free form of the 1Cl compound (Figure 3c). After removal of the guest molecules from the 1Cl·dioxane solvate, the system was collapsed to the guest free form of 1Cl, as indicated by the similarity between the simulated PXRD pattern of the guest free form of 1Cl and the experimental PXRD pattern of the apohost of 1Cl·dioxane solvate. The overlay diagram suggests that the transformation needs very small reorientation of the host molecules in the crystal lattice. The same guest free form was also produced upon guest removal from the other two types of solvates, namely, 1Cl·*p*-xylene and 1Cl·EtOAc (Figure 4).

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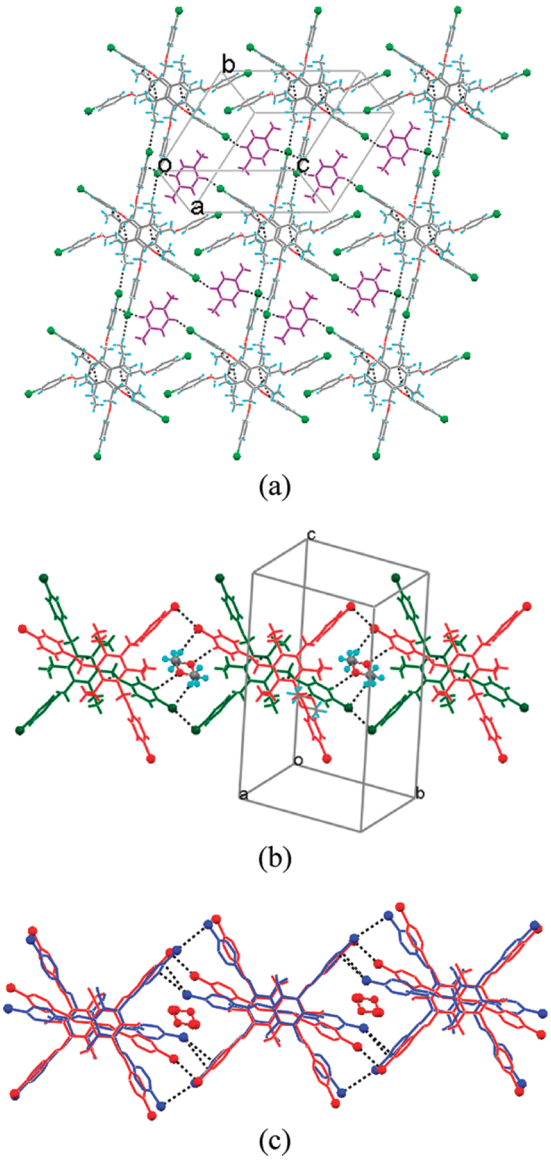

Figure 3. (a) Inclusion of *p*-xylene guests inside the cavities formed by 1Cl molecules in 1Cl·*p*-xylene, type HG5 system. (b) Enclathration of the dioxane guest molecules in the architecture of type HG6 made of 1Cl host molecules assembled via Cl···Cl dimer interactions in 1Cl·dioxane. (c) Overlay diagram of the guest free form of 1Cl (blue) and 1Cl·dioxane solvate (red) systems.

Interestingly, in all four different types of structures, HG1–4 observed in the 1I and 1Br solvates, the guest molecules reside inside the channel, which runs parallel to the crystallographic *a* axis (along the *b* axis in the case of picoline solvates), and the molecular tape, which is observed in the guest free form (GF1), is also observed in these clathrates. As a result, all these structures (GF1 and HG1–4) show two-dimensional (2-D) isostructurality[17] parallel to the *ab* plane, and they differ only in the interlayer contacts around the halogens. In the guest free form, GF1 and host–guest systems, HG1–4 and 6, the host molecules are assembled through inter-halogen interactions. The halogen groups form a type II dimer synthons in the GF1 and HG1 types of networks. When two such halogen dimers are further connected via a type-I inter-halogen interactions, a "Z" shape halogen tetramer synthon is formed in the HG2 type of networks, but when they are linked via two type-II inter-halogen interactions, a cyclic halogen tetramer motif is formed in the HG3 type of networks. On the other hand, in the network type HG4, the halogen dimers are connected via a type-II inter-halogen interactions to form a 1-D helical chain. Along with the inter-halogen interactions, the awkward shape of the molecules is also important in their diverse inclusion behavior in the solid state. In spite of the presence of several flexible bonds, the molecules show some kind of semirigidity in their "Y" shape conformation where the phenoxy planes are approximately perpendicular to the middle benzene ring.

The influence of a solvent molecule in the crystallization process is evident from the occurrence of polymorphism in a substance crystallized from different solvents.[18] It becomes even more important when a solvent molecule is incorporated in the crystal lattice.[19] The size, shape, functional group, etc. of a solvent could be a determining factor in the crystallization outcome. Nevertheless, it is very difficult to rationalize the role of a solvent molecule in terms of its property and the crystal structure of the solute. In this series of crystal structures, the systems more or less follow a general trend depending upon the types of solvent molecules used for crystallization. Small solvent molecules such as nitromethane, acetonitrile produced guest free form (GF1, 2) of the halogenated compounds. In the absence of a strong hydrogen bonding donor in the host molecule, pyridine behaves like benzene for 1I host (HG1). The HG2 type of network for the 1I/1Br hosts and the HG5 type of network for the 1Cl/1F hosts are generated when the solvent systems are chosen as methylated benzenes (toluene, *o*/*m*/*p*-xylene, mesitylene). The halogenated (chloroform, tetrachloromethane, dichloroethane and dibromoethane) and the cyclic ether (tetrahydrofuran and 1,4-dioxane) solvent systems produced an HG3 type of network for the 1I/1Br hosts. It is interesting to note that the halogenated solvent systems are quite different in sizes and shapes. On the other hand the picoline molecules, which are connected via C–H···N hydrogen bonds along the channel, guided 1I and 1Br to adopt an HG4 type of host network. Nevertheless, there are some exceptions, such as 1Br·pyridine and 1Br·*o*-xylene, which have chosen HG3 and HG1 networks instead of HG1 and HG2 types networks, respectively.

Isostructurality. Isostructurality is an important aspect in the crystal structures of the halogenated compounds. Saha et al. have performed a statistical analysis on the isostructurality in analogous halogen containing organic compounds on CSD version 5.26, February 2005 update.[13b] Herein we have extended the search on CSD version 5.31, August 2010 update, on reports of monovalent halogen (Cl, Br, and I) containing compounds, which are single component, not polymeric, no errors, no ions, no powder structures and $R < 0.10$ (Table S3, Supporting Information). Data analysis shows that in a total of 101 hits where all the three halogen derivatives (Cl, Br, and I) for the same compound are reported, 59.4% showed isostructurality among I and Br homologues, followed by 70.3% cases of Br and Cl isostructurality, and 28.7% cases showed a carryover of isostructurality in Cl, Br, and I analogues. Interestingly, there are also three sets of structures which show the isostructurality among all the four halogenated compounds. We have further searched to find out the possibility of an isostructurality in the clathrates of the halogenated compounds present in this data set. Interestingly, there is no hit where the guest free forms of the analogous chloro, bromo, and iodo compounds are isostructural as well as the clathrates of these compounds are also isostructural. Therefore, this is the first

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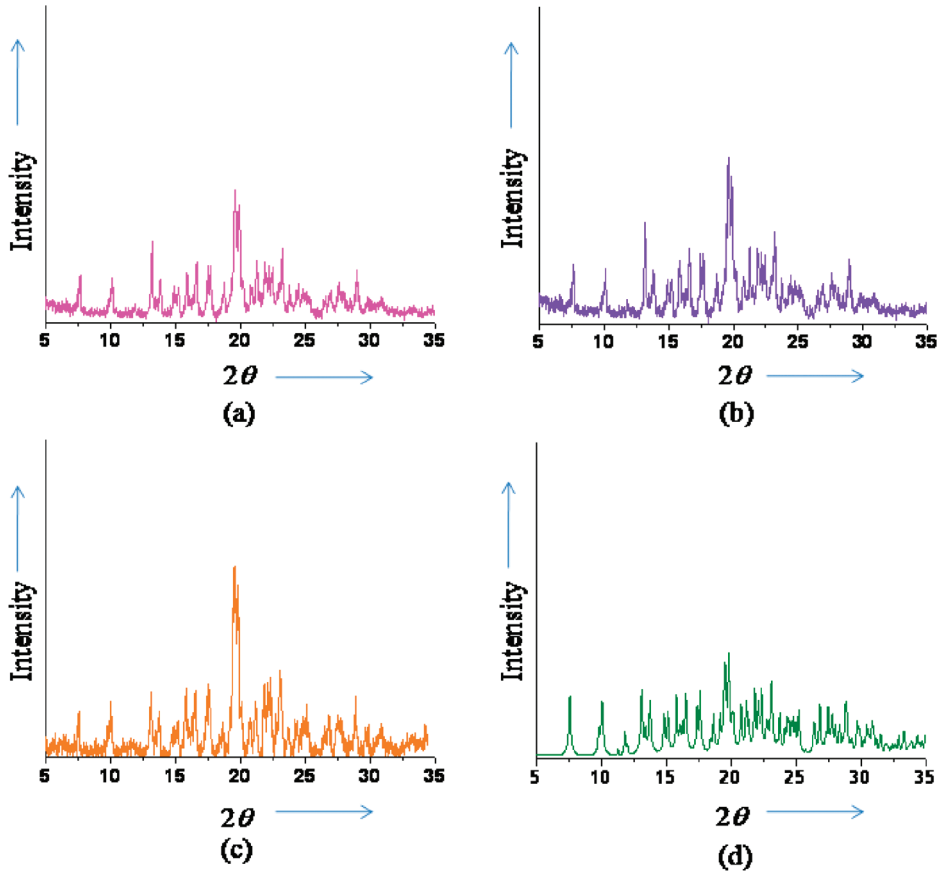

Figure 4. The PXRD plots for the apohosts of (a) 1Cl·EtOAc, (b) 1Cl·*p*-xylene, (c) 1Cl·dioxane, and (d) the simulated plot of the guest free form of 1Cl.

report where the guest free forms of the chloro, bromo, and the iodo compounds are isostructural and the clathrates of these compounds are also isostructural.

Thermal Analysis. Differential scanning calorimetry (DSC) experiments were performed to investigate the relative thermal stabilities of the different types of host−guest systems.[20] It is generally found that the thermal stability gradually decreases from the heavier to the lighter halocompounds.[13a] Among the isostructural 1:1 ethylacetate solvates in this series, the thermal stability of the 1I and 1Br solvates are comparable (desolvation temperature ∼ 86 °C), and as expected it is comparatively very low (desolvation temperature ∼ 58 °C) for the 1Cl solvate (Figure 5). Interestingly, in the cases of the dioxane and *p*-xylene solvates, not only the 1I clathrates are thermally more stable than the isostructural 1Br clathrates, but the structurally different 1Cl clathrates are also slightly more stable.

CONCLUSION

Hydrogen bonds are robust but the inter-halogen interactions are comparatively more flexible in nature. As a result, the halogen bond geometries can be altered easily to modify the voids which can accommodate guest molecules of different sizes and shapes. Structural analysis shows that the 1-D molecular tapes, which are guided by the inter-halogen interactions, are always present in the 1I and 1Br systems. On the contrary, this structural feature is present only in the guest free form and in the ethylacetate solvate, partially present in the dioxane solvate but absent in the toluene and *o/m/p*-xylene solvates of 1Cl. Therefore, the structural features and the thermal analysis of the systems suggest that inter-halogen interaction guided crystal packing is more favorable for the heavier halogens compared to the lighter halogens, which rather chooses C−H···hal hydrogen bond directed crystal packing as expected. Carbon bound iodo group is a better candidate for the halogen bonding compared to the other halogens, and the strength and the frequency of occurrence of such interactions decrease from iodo to fluoro gradually. Fluoro groups are mainly involved in weak hydrogen bonds. Our studies showed that the chloro group may behave like fluoro or heavier halogens depending upon the nature of the solvent/guest molecules. Similarities between the crystal structures of different host molecules also depend upon the guest molecules as shown in the cases of EtOAc, *p*-xylene, and pyridine clathrates in this series of structures. The molecules form several host architectures as well as easily form the guest free forms at ambient conditions. The awkward shapes of the molecules play an important role behind these interesting features. There are several reports on the isostructurality among the halogen compounds, but to the best our knowledge this is the first report where the guest free forms of the chloro, bromo, and iodo compounds are isostructural as well as a set of inclusion compounds are also isostructural. Therefore, these three halogens behave similarly in different packing arrangements of the host molecules.

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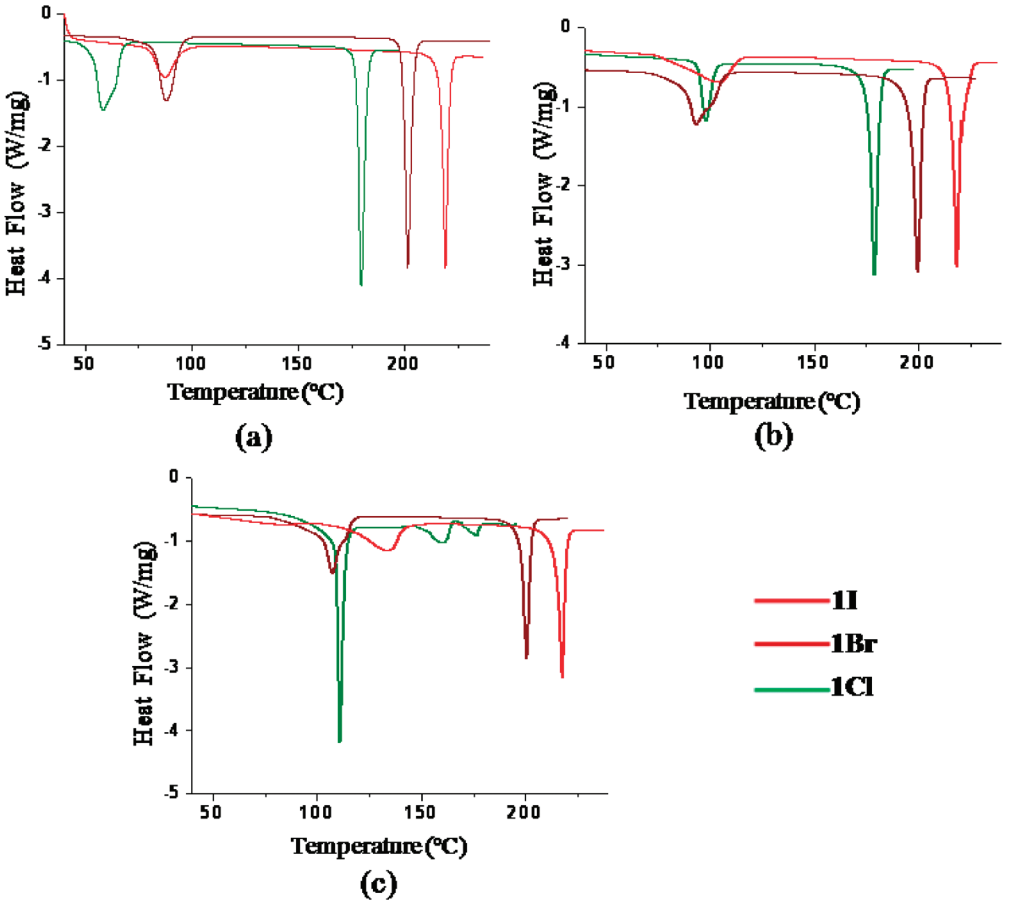

Figure 5. (a) DSC plots for isostructural 1X·EtOAc solvates. (b) DSC plots for 1X·dioxane solvates (X = I and Br are visostrcutural). (c) DSC plots for 1X.p-xylene solvates (X = I and Br are isostructural). The first endotherm in each case signifies desolvation of the system.

EXPERIMENTAL SECTION

Synthesis: 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene. 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene was prepared according to the procedure mentioned in the literature.[21]

1,3,5-Triethyl-2,4,6-tris(4-halophenoxy)methylbenzenes (1X). KOH (5 equiv, 11.3 mmol, 655.4 mg) and 4-X-phenol (5 equiv, 11.3 mmol) were dissolved in 100 mL of tetrahydrofuran and stirred for 1 h. 1 g (2.2 mmol) of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene was then added to the solution and stirred for 48 h under reflux. The solvent was removed in vacuo. Water (100 mL) was added to the mixture and the 1X compound was extracted with dichloromethane (3 × 50 mL). The dichloromethane was removed under a vacuum to obtain the required compound. The compounds are characterized by ^{1}H and ^{13}C NMR. The detailed characterization is given as follows:

1I. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.216 (9H, t, 7.6 Hz), 2.792 (6H, q, 7.6 Hz), 5.036 (6H, s), 6.820 (6H, d, 8.2 Hz), 7.593 (6H, d, 8.2 Hz). ^{13}C NMR δ 16.53, 23.14, 64.42, 117.11, 130.96, 131.33, 138.53, 146.48, 158.91. M.P. 217−219 °C.

1Br. ^{1}H NMR($CDCl_3$, 400 MHz) δ 1.228 (9H, t, 7.6 Hz), 2.806 (6H, q, 7.6 Hz), 5.047 (6H, s), 6.920 (6H, d, 8.8 Hz), 7.430 (6H, d, 8.8 Hz). ^{13}C NMR δ 16.54, 23.14, 64.55, 116.49, 129.05, 130.98, 132.55, 146.46, 158.13. M.P. 201−203 °C.

1Cl. ^{1}H NMR($CDCl_3$, 400 MHz) δ 1.228 (9H, t, 7.6 Hz), 2.808 (6H, q, 7.6 Hz), 5.048 (6H, s), 6.960 (6H, d, 8.1 Hz), 7.286 (6H, d, 8.1 Hz). ^{13}C NMR δ 16.56, 23.15, 64.59, 115.94, 129.06, 131.01, 134.81, 146.44, 157.61. M.P. 176−178 °C.

1F. ^{1}H NMR($CDCl_3$, 400 MHz) 1.25 (9H, t, 7.6 Hz), 2.84 (6H, q, 7.6 Hz), 5.05 (6H, s), 6.98 (6H, dd, 8.8, 4.4 Hz), 7.03 (6H, t, 8.8 Hz) ^{13}C NMR: 16.44, 20.94, 64.73, 115.42, 116.04, 128.9, 131.03, 146.19, 155.03. M.P. 155−157 °C.

1Me. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.245 (9H, t, 7.2 Hz), 2.328 (9H,s), 2.847 (6H, q, 7.2 Hz), 5.060 (6H, s), 7.041 (6H, d, 8.0 Hz), 7.052 (6H, d, 8.0 Hz). ^{13}C NMR δ 16.61, 20.64, 23.11, 64.29, 114.51, 130.11, 130.3, 131.33, 146.23, 157.01. M.P. 142−144 °C.

Crystallization. Diffraction quality single crystals were obtained by dissolving the compounds in a suitable solvent followed by slow evaporation of the solvent at room temperature. The solvates were obtained from the corresponding solvents used for crystallization. The guest free forms of the 1I and 1Br compounds were obtained from acetonitrile solvent, and the guest free forms of the 1Cl, 1F, and 1Me compounds were obtained from chloroform, ethylacetate, and dimethylformamide solvents, respectively.

X-ray Crystallography. X-ray crystal data were collected on a Xcalibur Eos Diffraction Ltd. with Mo−K_α radiation (λ = 0.71073 Å). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied.[22] Structure solution and refinement were performed with SHELXS-97[23] and XL,[24] respectively. Wherever the highly disordered guest molecules could not be modeled, the SQUEEZE routine of PLATON was used to treat the residual electron density.[25] Pertinent crystallographic data collection and refinement parameters of some representative systems are shown in Table 2 and for the rest of the systems and the intermolecular interaction parameters of the systems are shown in Tables S1 and S2, respectively, in Supporting Information.

Powder Diffraction Experiments. The PXRD spectrum of the apohosts of 1Cl clathrates were recorded at room temperature using Cu Kα radiation (λ = 1.54056 Å) from X-ray diffractometer (model: X-pert Panalytical). The spectrum was recorded with 2θ ranging from 2° to 45° and a step size of 0.02°. The apohosts of the 1Cl clathrates were prepared by grinding the clathrate crystals manually in a mortar pestle, followed by heating under a vacuum at 150−155 °C.

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Table 2. Crystallographic Data for Some Selected Systems[a]

system	1I (GF1)	1I·pyridine (HG1)	1I·EtOAc (HG2) (squeezed)	1I·dioxane (HG3)	1I·picoline (HG4)
formula	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3{\cdot}C_6H_5N_1$	$C_{33}H_{33}I_3O_3{\cdot}C_4H_8O_2$	$C_{33}H_{33}I_3O_3{\cdot}C_4H_8O_2$	$C_{33}H_{33}I_3O_3{\cdot}C_6H_7N$
M_r	858.29	937.39	946.40	946.40	951.45
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.9115(9)	9.9646(6)	9.8411(3)	9.9745(8)	13.3699(7)
b (Å)	13.3645(11)	13.3987(7)	13.2260(5)	13.3547(8)	9.8382(6)
c (Å)	24.952(3)	14.6107(8)	15.5234(6)	15.7276(13)	28.8159(18)
α (°)	90.00	90.411(5)	111.333(4)	113.199(7)	90.00
β (°)	93.168(9)	107.322(5)	94.651(3)	97.615(7)	90.815(6)
γ (°)	90.00	90.923(5)	91.720(3)	90.585(6)	90.00
V (Å^3)	3300.2(6)	1861.85(18)	1872.00(12)	1904.2(2)	3789.9(4)
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)
Z	4	2	2	2	4
F(000)	1656	912	828	924	1856
μ (mm^{-1})	2.871	2.553	2.531	2.500	2.510
ref collected/unique	9062/3014	10273/5020	10242/3479	10504/4776	9568/5424
parameters	374	428	364	398	436
final R indices [$I > 2\sigma(I)$]	R_1 = 0.045	R_1 = 0.066	R_1 = 0.045	R_1 = 0.072	R_1 = 0.047
R indices (all data)	wR_2 = 0.112	wR_2 = 0.174	wR_2 = 0.084	wR_2 = 0.231	wR_2 = 0.116
goodness of fit on F^2	0.787	1.039	0.726	1.031	1.020

system	1Br (GF1)	1Br·EtOAc (HG2) (squeezed)	1Cl (GF1)	1Cl·*p*-xylene (HG5)	1Cl·dioxane (HG6)
formula	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3{\cdot}C_4H_8O_2$	$C_{33}H_{33}Cl_3O_3$	$C_{33}H_{33}Cl_3O_3{\cdot}(C_8H_{10})_2$	$C_{33}H_{33}Cl_3O_3{\cdot}(C_4H_8O_2)_{0.5}$
M_r	717.33	805.43	583.94	690.14	628.00
crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	19.1740(6)	9.8164(17)	28.8875(11)	10.4401(10)	10.1834(3)
b (Å)	13.3687(4)	13.4010(16)	13.4670(4)	15.6190(13)	13.5610(4)
c (Å)	25.1912(9)	14.992(3)	24.9657(11)	16.1505(15)	23.4243(7)
α (°)	90.00	110.825(14)	90.00	64.153(9)	90.00
β (°)	109.733(4)	92.594(15)	110.691(5)	71.764(9)	91.118(3)
γ (°)	90.00	90.180(12)	90.00	77.321(8)	90.00
V (Å^3)	6078.1(3)	1841.1(5)	9085.9(6)	2240.4(4)	3234.21(17)
T (K)	298(2)	298(2)	298(2)	298 (2)	298 (2)
Z	8	2	12	2	4
F(000)	2880	720	3672	844	1320
μ (mm^{-1})	4.014	3.313	0.334	0.244	0.320
ref collected/unique	16564/6466	10058/2915	24827/6644	10409/2108	7547/5689
parameters	709	364	1064	503	382
final R indices [$I > 2\sigma(I)$]	R_1 = 0.048	R_1 = 0.054	R_1 = 0.123	R_1 = 0.062	R_1 = 0.053
R indices (all data)	wR_2 = 0.090	wR_2 = 0.144	wR_2 = 0.412	wR_2 = 0.126	wR_2 = 0.113
goodness of fit on F^2	0.823	0.818	1.029	0.737	1.059

system	1Cl·EtOAc (HG2) (squeezed)	1F (GF2)	1Me (GF3)
formula	$C_{33}H_{33}Cl_3O_3{\cdot}C_4H_8O_2$	$C_{33}H_{33}F_3O_3$	$C_{36}H_{42}O_3$
M_r	672.08	534.59	522.70
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	9.7072(8)	10.757(5)	10.3507(7)
b (Å)	13.4028(9)	18.021(7)	19.1256(12)
c (Å)	14.6608(14)	14.908(5)	15.2676(12)
α (°)	110.951(7)	90.00	90.00
β (°)	91.936(7)	104.84(4)	96.584(7)
γ (°)	90.081(6)	90.00	90.00
V (Å^3)	1780.1(3)	2793.6(19)	3002.5(4)
T (K)	298 (2)	298(2)	298(2)
Z	2	4	4
F(000)	612	1128	1128
μ (mm^{-1})	0.284	0.093	0.072
ref collected/unique	6339/3262	6099/1033	7019/2649
parameters	374	355	358
final R indices [$I > 2\sigma(I)$]	R_1 = 0.078	R_1 = 0.088	R_1 = 0.074

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Table 2. continued

system	1Cl·EtOAc (HG2) (squeezed)	1F (GF2)	1Me (GF3)
R indices (all data)	wR_2 = 0.263	wR_2 = 0.115	wR_2 = 0.195
goodness of fit on F^2	1.008	0.774	0.991

[a]The rest of the systems are given in Supporting Information.

Thermal Experiments. TG-DSC experiments were performed in a TA Instruments. Crystals taken from the mother liquor were dried on a tissue paper and placed in crimped but vented aluminum sample pans for DSC experiment. The amount of sample taken varied from 4 to 7 mg in each case. The sample was heated from 30 to 250 °C for 1I solvates, 30 to 220 °C for 1Br solvates, and 30 to 200 °C for 1Cl solvates at a rate of 10 °C/min.

NMR Experiments. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance-II spectrometer

■ ASSOCIATED CONTENT

Supporting Information

Isostructural packing in the guest free forms and the clathrate structures (Figure S1), ORTEP and crystallographic refinement details for disordered molecules (Figure S2), crystallographic data and refinement parameters (Table S1), the intermolecular interaction parameters (Table S2), and CSD search on isostructural halogenated organic molecules (Table S3) are available. Crystallographic data in CIF are available. CCDC 856123−856165 contain the supplementary crystallographic data for this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

Dedicated to Prof. T. N. Guru Row on the occasion of his 60th birthday.

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