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pK_a-Directed Host–Guest Assemblies: Rational Analysis of Molecular Adducts of 2,4-Diamino-6-methyl-1,3,5-triazine with Various Aliphatic Dicarboxylic Acids

Amit Delori,[a] Eringathodi Suresh,[b] and V. R. Pedireddi*[a]

Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday

Abstract: Molecular adducts of 2,4-diamino-6-methyl-1,3,5-triazine (**1**) have been prepared with various aliphatic dicarboxylic acids. The molecular complexes (**1a**–**1i**) thus formed by co-crystallizing **1** with oxalic, malonic, succinic, fumaric, acetylene dicarboxylic, glutaric, thiodiglycolic, diglycolic, and adipic acids have been found to give two types of host–guest assemblies that have voids or channels in a three-dimensional arrangement. The different types of host–guest arrangement appear to result from differences in the acidity of the dicarboxylic acids, that is, acids with p$K_a < 3.0$ give host networks that consist of **1** and the corresponding acid with water or solvent molecules of crystallization present as guests, whereas acids with p$K_a > 3.0$ exist as guests in voids in a host network formed by **1**. The former arrangement is observed in adducts **1a**, **1b**, **1e**, and **1h** and the latter arrangement is found in adducts **1c**, **1d**, **1f**, **1g**, and **1i**.

Keywords: dicarboxylic acids · host–guest systems · hydrogen bonds · molecular recognition · supramolecular chemistry

Introduction

Supramolecular synthesis[1] by co-crystallizing compounds that have complementary functional groups is a general process to obtain assemblies of varied architectures, as demonstrated by numerous examples in recent literature.[2] Of particular interest are the complexes formed by various aza-donor compounds, such as triazines, pyrimidines, and pyridines, with compounds that have functionalities like −COOH, amides, and cyclic imides.[3] Among these, the "rosette" network structure with 18 hydrogen bonds that is formed by melamine (1,3,5-triaminotriazine) and cyanuric acid serves as a representative example to demonstrate the collective strength of noncovalent bonds.[4] Furthermore, the assemblies formed by symmetrically substituted molecules, such as trimesic acid (benzene-1,3,5-tricarboxylic acid), with various complementary molecules exemplify the elegance of the molecular recognition process for the creation of a variety of architectures with cavities and channels.[5]

One of the salient features of these studies is the formation of host–guest type assemblies[6] that give distinct supramolecular networks through different types of hydrogen bond.[7,8] However, in many assemblies the hydrogen bonds were found to be ionic owing to the transfer of protons, which is especially observed in the assemblies formed between carboxylic acids and aza-donor compounds. This was attributed to pK_a differences between the constituents, rather than structural demand.[9] In parallel, Aakeröy and co-workers have made use of the pK_a concept for the preparation of directed multiple-component supramolecular assemblies.[10] Thus, the pK_a of the compounds under consideration appears to be a significant feature that should be studied, so that further insights into the mechanism of the synthesis of directed assemblies through a molecular recognition process can be obtained. The outcome of such studies would be of immense utility in the further development of recently evolved co-crystallization studies that employ pharmaceutically important molecules[11] because many of the co-crystallizing agents are carboxylic acids, particularly ali-

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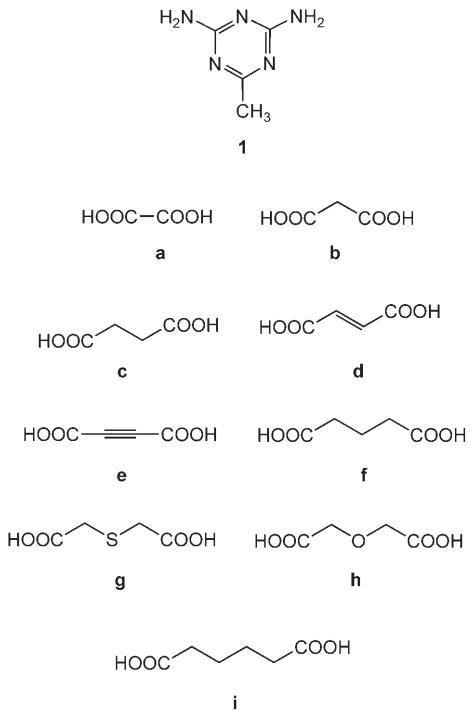
phatic dicarboxylic acids, such as malonic, succinic, or adipic acid. As a consequence, we are interested in synthesizing numerous supramolecular assemblies that primarily possess −COOH and aza-donor moieties to deduce the salient features of recognition patterns in terms of the pK_a of the constituents.

Herein, we have initiated our studies by investigating the co-crystallization of 2,4-diamino-6-methyl-1,3,5-triazine (**1**) with various aliphatic dicarboxylic acids that differ by methylene or analogous groups, as shown in Scheme 1. The complexes **1a**–**1i** thus obtained were analyzed by single-crystal X-ray diffraction studies to evaluate the structures in terms of their recognition patterns, three-dimensional packing arrangements, and so forth, and these salient features will be discussed in following sections.



Scheme 1. Structures of **1** and the dicarboxylic acids used in this investigation.

Results and Discussion

Complexes **1a**–**1i** were prepared by co-crystallizing **1** with oxalic, malonic, succinic, fumaric, acetylene dicarboxylic, glutaric, thiodiglycolic, diglycolic, and adipic acids, respectively, in CH_3OH. The solid-state structures of the complexes have several common features and distinct differences. To understand and rationalize the structural features of the complexes, the salient features of each complex are illustrated herein and comparisons are made among the structures.

Solid-state structure of 1: Single crystals were obtained from a solution of **1** in CH_3OH upon slow evaporation, and structure determination revealed that the asymmetric unit also has solvent molecules of crystallization. Nonetheless, the packing of the molecules in three dimensions is quite intriguing and forms a host–guest type assembly (Figure 1).

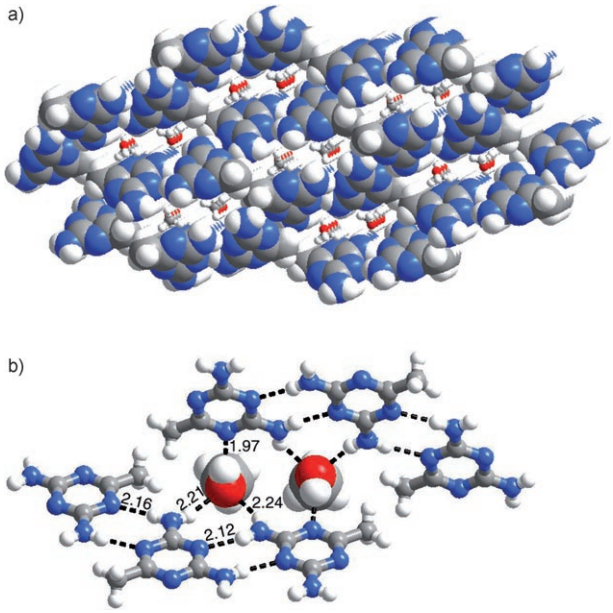


Figure 1. a) Three-dimensional packing arrangement of the molecular adduct of **1** and CH_3OH that shows the channels being occupied by CH_3OH molecules. b) Detail of interactions between the molecules in a typical channel.

In this arrangement, molecules of **1** self-assemble through N−H···N hydrogen bonds and hydrophobic interactions that form the host network, with CH_3OH molecules residing in the channels thus produced. Around each channel, six molecules of **1** arrange as two triads held together by hydrophobic interactions, and within each triad the molecules are connected by two different centrosymmetric N−H···N hydrogen-bonded moieties (2.12 and 2.16 Å). Furthermore, the CH_3OH molecules interact with the host lattice by forming N−H···O (2.21 and 2.24 Å) and O−H···N (1.97 Å) hydrogen bonds. Thus, the structure of **1** itself is quite intriguing and suggests that it has the ability to form host–guest systems, which corroborates the aims of this endeavor.

Solid-state structure of 1 and oxalic acid (1a): Co-crystallization of oxalic acid and **1** in CH_3OH resulted in the formation of a complex of **1**/oxalic acid (2:1) along with solvent molecules of crystallization. In the three-dimensional packing of **1a**, the molecules are arranged in the form of stacked sheets (Figure 2).

Of the two −COOH groups of oxalic acid, only one is deprotonated. The −COOH group forms a O−H···N (1.83 Å) and N−H···O (2.06 Å) pair-wise cyclic hydrogen-bonding pattern, whereas the $-COO^-$ group forms two single N−

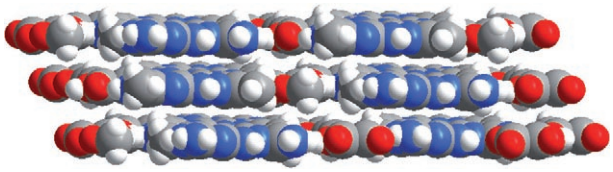


Figure 2. Packing arrangement showing the stacked sheets in the crystal structure of **1a**.

H···O$^-$ hydrogen bonds (1.88 and 1.98 Å) with the molecules of **1**.

Furthermore, molecules of **1** interact with each other to form crinkled molecular tapes, as shown in Figure 3, by three different types of cyclic pair-wise N–H···N hydrogen bonds with lengths in the range of 2.10 to 2.50 Å (Figure 3). In the two-dimensional arrangement, adjacent tapes of **1** are separated by oxalic acid molecules to give voids that are occupied by the CH_3OH solvent molecules of crystallization (Figure 3b). As a result, six molecules of **1** are arranged as two triads around each void, exactly like the CH_3OH adduct of **1**, with the only difference being that instead of hydrophobic interactions, the triads are held together by oxalic acid molecules. However, unlike the CH_3OH adduct of **1**, the voids in the three-dimensional arrangement of **1a** do not align because the adjacent sheets are staggered (see Figure 3c) and as a consequence of this, channels along a crystallographic axis could not be established.

Solid-state structure of 1 and malonic acid (1b): Crystals of complex **1b** (**1**/malonate, 2:1) were obtained from a solution of **1** and malonic acid in CH_3OH, along with four molecules of water. Unlike complex **1a**, both –COOH groups were deprotonated in **1b**, which we will discuss in detail in a later section. In three dimensions, complex **1b** also forms a host–guest type assembly with the host being constituted by molecules of **1** and malonate, as shown in Figure 4. Therefore, the channels observed in **1b** are filled with water molecules.

The interactions between the molecules of **1** and malonate around each channel have some resemblance to those in **1a** but differ greatly with respect to the interaction between the molecules of **1**. Although two triads have been noted in **1b**, as in the CH_3OH adducts of **1** and **1a**, the interaction between the molecules within the triads is not same as that observed in **1** and **1a**. Within each triad in **1b**, the molecules are held together by cyclic and single N–H···N hydrogen bonds with lengths of 2.13 and 2.23 Å, respectively. These triads are further held together by malonate molecules through N^+–H···O$^-$ and N–H···O$^-$ hydrogen bonds (1.80 and 1.91 Å). Water molecules exist in the channels as chains (Figure 4c) formed through O–H···O hydrogen bonds (1.83 and 2.00 Å), which are in turn connected to the host network through N–H···O (2.02 Å) and O–H···O$^-$ (1.88 and 1.92 Å) hydrogen bonds with **1** and malonate, respectively, as shown in Figure 4b.

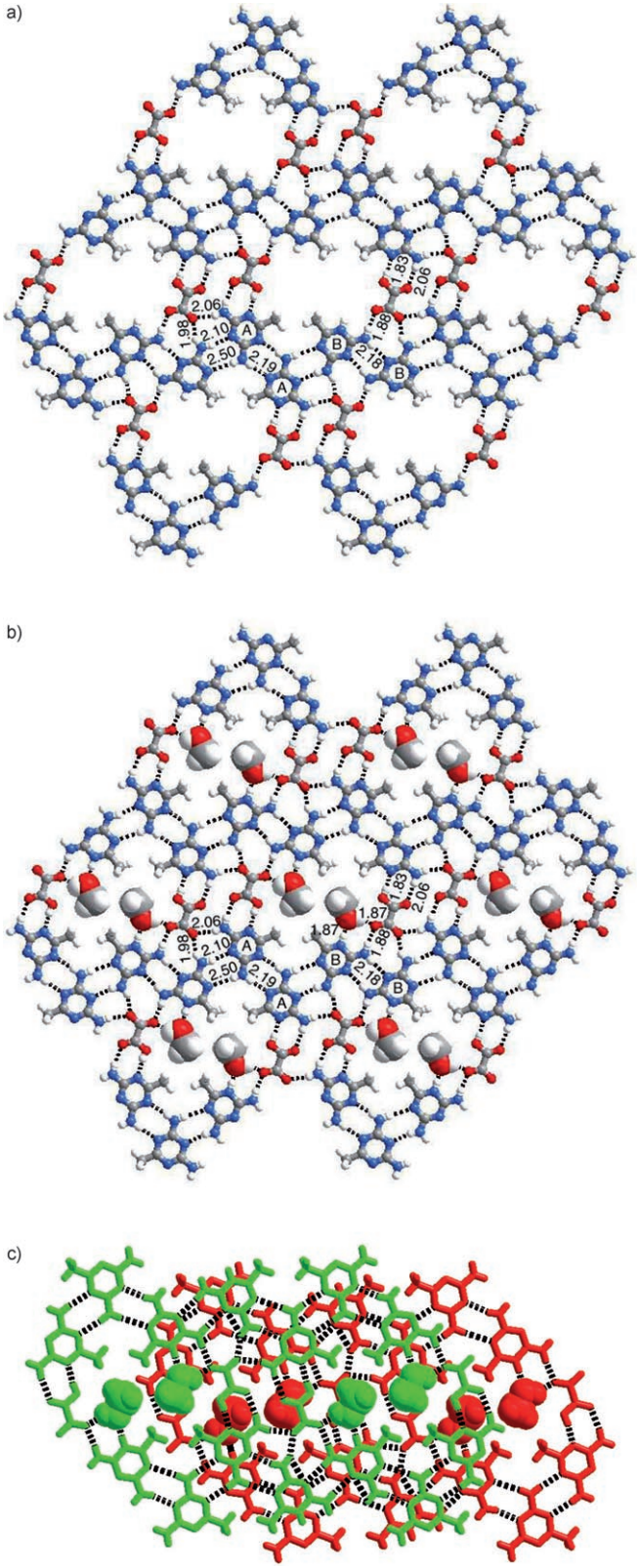


Figure 3. a) Arrangement of molecules in a typical sheet observed in **1a**, with cavities formed by **1** and oxalic acid. b) CH_3OH molecules (solvent of crystallization) in the voids observed in a). c) The staggered stacking of adjacent sheets in the crystal structure of **1a**.

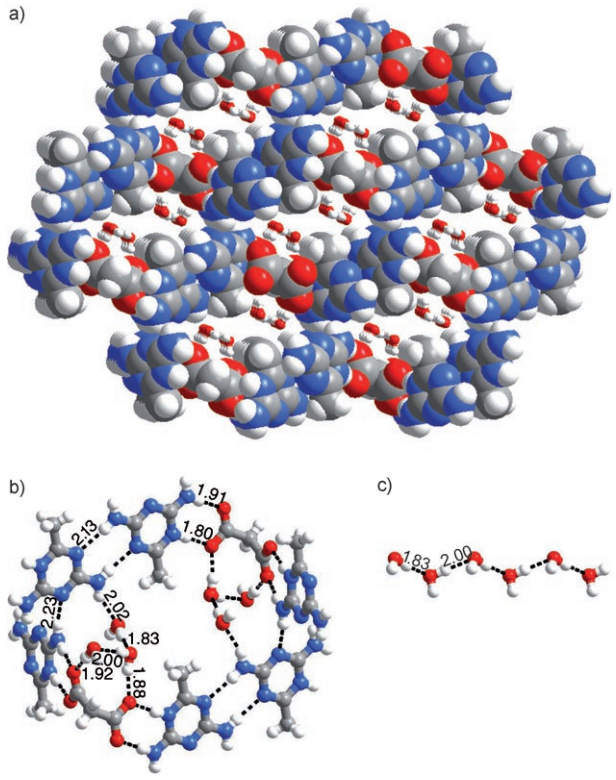


Figure 4. a) The host–guest network observed in **1b**, with the channels filled by water molecules. b) Recognition pattern between **1** and malonate. c) Interaction between neighboring water molecules in each channel.

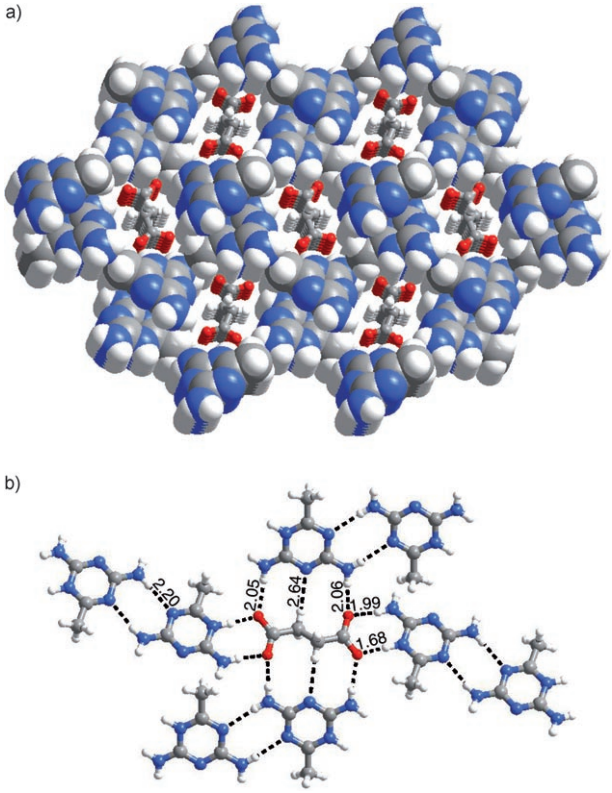


Figure 5. a) The host–guest network observed for **1c**, with the host network being formed by molecules of **1** and the resulting channels being occupied by succinate molecules. b) The arrangement of molecules around each channel, showing different types of interactions between **1** and succinate.

Solid-state structure of 1 and succinic acid (1c): In the structure of **1c** formed between **1** and succinic acid, no water or solvent molecules of crystallization are present, but succinic acid exists as succinate owing to the deprotonation of both −COOH groups, as observed for malonic acid in **1b**. Although complex **1c** forms a host–guest type assembly in three dimensions, as shown in Figure 5a, the host is formed entirely by molecules of **1**, unlike complexes **1a** and **1b**, and the resultant channels are occupied by succinate molecules. Furthermore, detailed analysis of the host network reveals that around each channel, the molecules of **1** exist as dimers, not triads as noted in **1a** and **1b**, with the formation of cyclic N−H···N hydrogen bonds with a length of 2.20 Å (Figure 5b). These dimers, in turn, interact with succinate molecules to form N^{+}−H···O^{-} and N−H···O^{-} hydrogen bonds and the corresponding lengths are 1.68 and 1.99 Å, respectively. In addition, a striking feature is the triple hydrogen bonding pattern between the constituents, which consist of N−H···O^{-} (2.05 Å), C−H···N (2.64 Å), and N−H···O^{-} (2.06 Å) hydrogen bonds (Figure 5b). It seems that this type of pattern has evolved due to the complementary distance between the acceptors and donors on **1** and the succinate molecules as the distance of 5.04 Å between the O atoms at each end of succinate matches with the distance of 4.63 Å between the H atoms of the NH_2 groups at the *meta* positions of **1**. Such a pattern is not possible in **1a** and **1b** because the corresponding distances between the O atoms on oxalic and malonic acid (2.73/2.65 and 3.57 Å, respectively) are not complementary with the distance between the NH_2 groups on **1**.

To draw further insights into the different types of host networks observed in **1a**–**1c**, complexes of **1** with several other dicarboxylic acids have been prepared, as described below.

Solid-state structure of 1 and fumaric acid (1d): Complex **1d** is isostructural with **1c**, with **1** and fumarate molecules organized in a ratio of 2:1. The packing of molecules in three dimensions and the interactions between the molecules are shown in Figure 6. The similarity between **1c** and **1d** can be certainly attributed to the similar dimensions of succinic and fumaric acids, even though the latter has different hybridization features (sp^2 instead of sp^3) for the carbons between the −COOH groups, thus highlighting the importance of the geometrical features of the molecules and placement of the complementary functional groups.

Solid-state structure of 1 and acetylene dicarboxylic acid (1e): The molecular adduct of **1** and acetylene dicarboxylic acid, obtained from a methanolic solution, crystallizes as a monohydrate. This complex, which was expected to be simi-

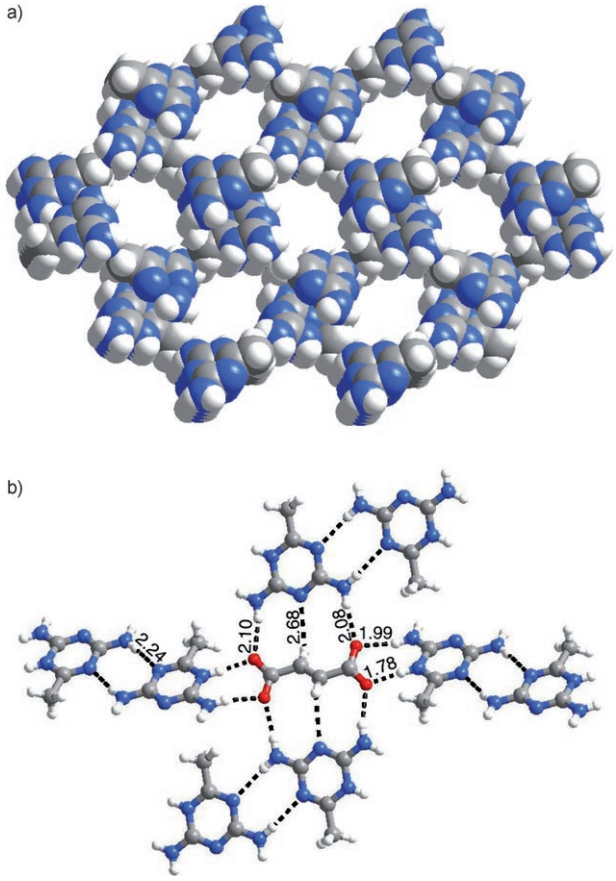


Figure 6. a) Host network created by the molecules of **1** in **1d**. b) Arrangement of **1** and fumarate in **1d**.

lar to **1c** and **1d** based on geometrical considerations of the acid molecules, gave a structure similar to **1a**, which is perhaps due to the linear geometry of acetylene dicarboxylic acid being similar to oxalic acid. The three-dimensional arrangement of **1e** forms a stacked sheet structure, which is shown in Figure 7a.

In a typical sheet, the molecules arrange in a manner such that both **1** and acetylene dicarboxylate molecules form the host-network cavities. The molecules of **1** interact with each other through N–H···N hydrogen bonds with lengths of 2.17 and 2.18 Å (see Figure 7b), which result in an infinite tape network with carboxylate molecules glued to these tapes like pendants through the formation of N^+–H···O^- (1.81 Å) and N–H···O^- (1.99 Å) hydrogen bonds. In two dimensions, the adjacent units are arranged to create void spaces that are occupied by water molecules and dimers of **1**. Furthermore, the sheets around each channel are not aligned along a crystallographic axis, thus no channels are observed in the three-dimensional arrangement. Overlapped adjacent sheets are shown in Figure 7c.

Solid-state structures of 1 with glutaric and thiodiglycolic acids (1f and 1g): Complexes **1f** and **1g** were prepared from solutions of **1** with glutaric or thiodiglycolic acids, re-

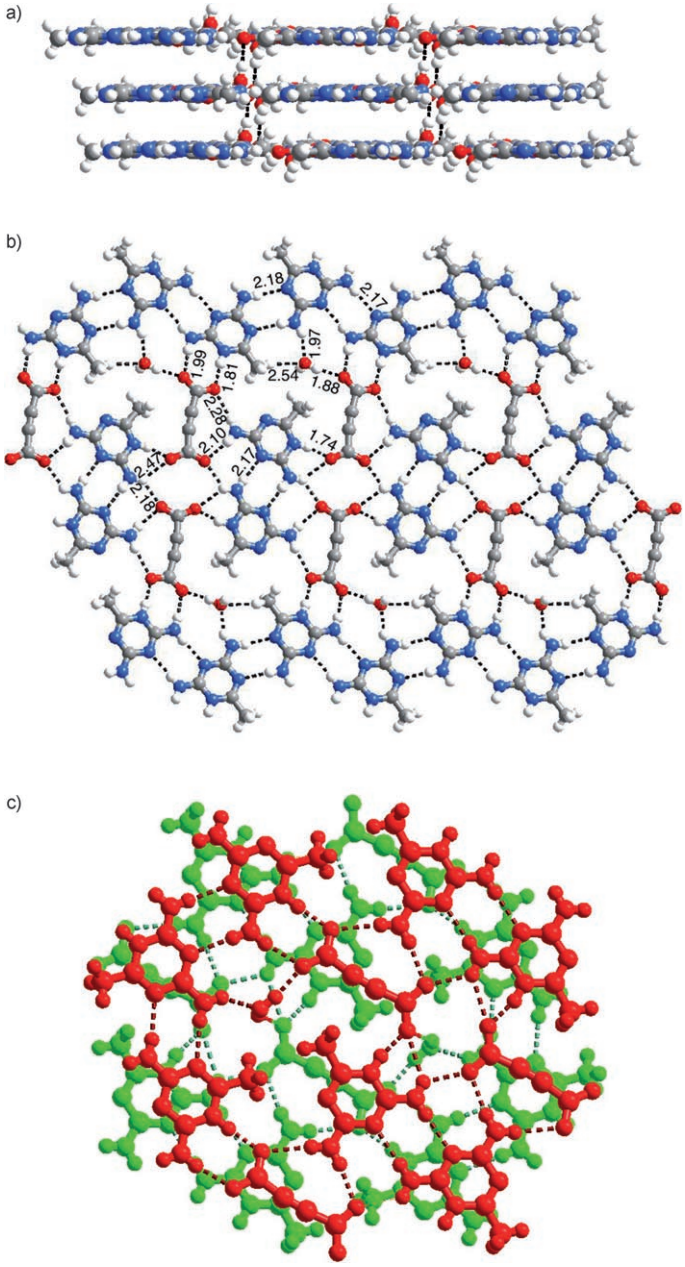


Figure 7. a) Stacking of planar sheets in the three-dimensional arrangement in **1e**. b) Annotation of the intermolecular interactions observed within the sheet structure of **1e**. c) Overlap of adjacent sheets in the crystal structure of **1e**.

spectively, in CH_3OH. Single-crystal X-ray diffraction analysis revealed that both are isostructural and form host–guest type assemblies, with **1** forming the host network (Figure 8a) as also observed in **1c** and **1d**, and glutarate or thiodiglycolate occupying the channels as guest species. Unlike the situation in **1c** and **1d**, there is no triplet hydrogen-bonding pattern observed in **1f** and **1g**, as shown in Figure 8b and c.

Solid-state structure of 1 and diglycolic acid (1h): Although diglycolic acid is structurally similar to glutaric and thiodiglycolic acid, it is quite interesting to note that **1h** did not

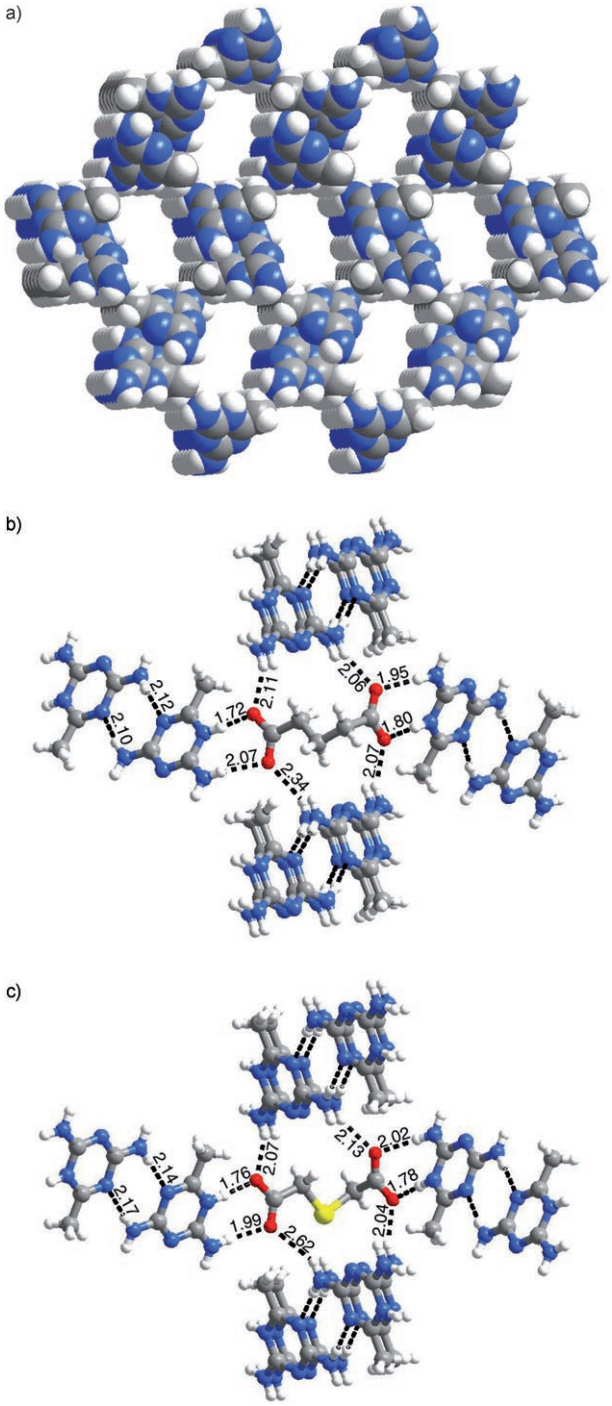


Figure 8. a) Host network formed by **1** in complexes **1f** and **1g**. b,c) Arrangement of molecules of **1** and glutaric acid or thiodiglycolic acid in **1f** and **1g**, respectively.

show isostructurality with the structures of either **1f** or **1g**. However, the three-dimensional packing of **1h** as a host–guest assembly (Figure 9) somewhat resembles **1b**. Furthermore, detailed analysis of the exact nature of the interaction between the molecules revealed a rather exotic triple-helix structure, as shown in Figure 10a. Intermolecular interactions between the helices in the triple helix and within each

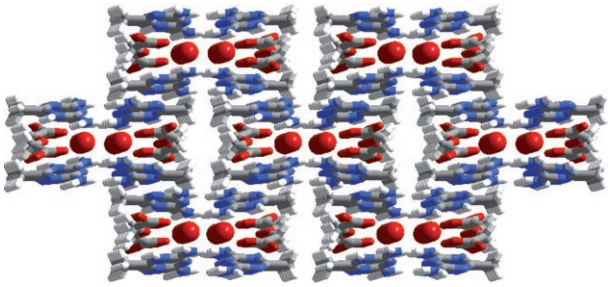


Figure 9. Packing of molecules in the three-dimensional arrangement of **1h**.

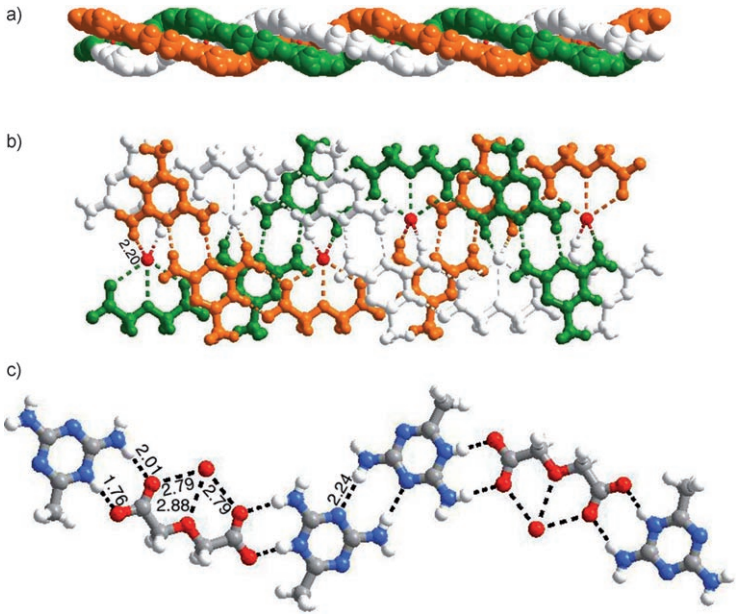


Figure 10. a) Triple helix observed in the structure of **1h**. b) Interactions between the helices in the triple helix. c) Interactions between the molecules within a helix.

helix are shown in Figure 10b and c. Each helix is formed through molecular recognition between **1** and diglycolate by cyclic N–H···O^- and N^+–H···O^- hydrogen-bonding patterns (Figure 10c). Furthermore, molecules of **1** exist as dimers formed by cyclic N–H···N hydrogen-bonding interactions and the different helices interact with each other through water molecules.

Solid-state structure of 1 and adipic acid (1i): Crystals obtained from a solution of **1** and adipic acid in CH_3OH were found to be a molecular complex of **1**/adipic acid (2:1); its molecular arrangement is shown in Figure 11. In fact, the structure is very similar to **1f** and **g** except for the acid moiety.

In addition, the three-dimensional arrangement of **1i** highlights the formation of a host–guest assembly with molecules of **1** as the host and adipic acid as the guest molecules that occupy the channels created by **1** (Figure 12).

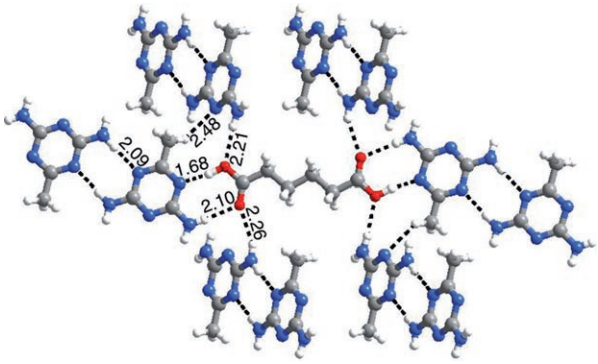


Figure 11. Interactions between **1** and adipic acid in **1i**.

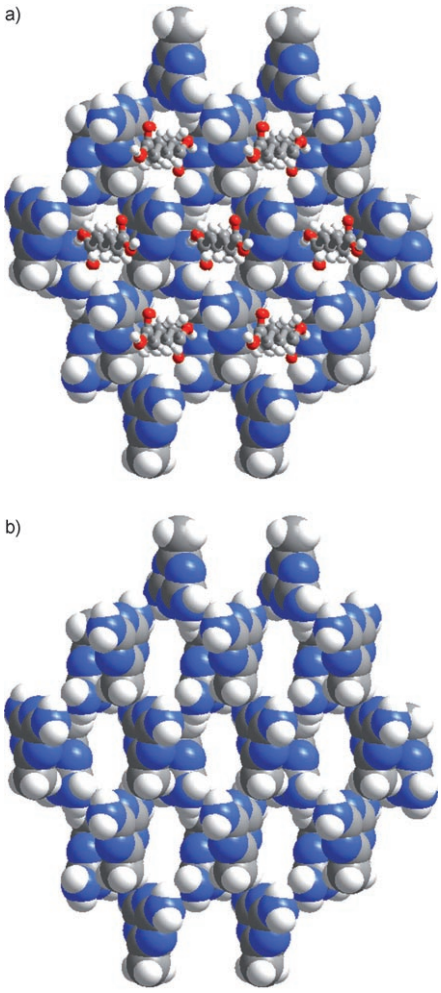


Figure 12. a) Three-dimensional packing of molecules in **1i**. b) Clear visualization of the channels in **1i** without the acid molecules.

The structure of **1i** is reminiscent of **1c** and **1d**, but in terms of the interaction between adipic acid and **1** it resembles **1f** and **1g**. Another interesting feature is that **1i** is the first example in this series in which the dicarboxylic acid did not undergo proton transfer. Therefore, adipic acid interacts with **1** through O–H···N and N–H···O hydrogen bonds with lengths of 1.68 and 2.10 Å, respectively.

Thus, analysis of structures **1a–1i** suggests that in addition to the complementary recognition abilities, such as size, shape, and position, additional features from recognition patterns to the ultimate topological arrangements must be playing significant roles, and for this reason, correlations between structures **1a–1i** and the CH_3OH adduct of **1** have been considered.

Structural correlations between structures 1a–1i: A comparison of structures **1a–1i** highlights the ability of **1** to form a host network in the presence of a variety of molecules, ranging from simple CH_3OH molecules to lengthy molecules like adipic acid. However, the host network was only able to create voids in **1a** and **1e**, but produced channels in the remaining structures (**1b–1d**, **1f–1i** and the CH_3OH adduct of **1**). A striking feature of these host–guest assemblies is that the host networks in **1a**, **1b**, **1e**, and **1h** are formed by both **1** and the corresponding acid/carboxylate molecules with the voids/channels being filled by either water or solvent molecules of crystallization, whereas in **1c**, **1d**, **1f**, **1g**, and **1i**, such a network is formed by **1** only and the carboxylate/acid moieties reside in the channels as guests. As we visualize the progress of structures from **1a**→**1i**, the dicarboxylic acids in this series are arranged in ascending order of increasing methylene groups or analogues, but the observed variations in the resulting host–guest arrangements did not bear any direct correlation with this property. Although the majority of dicarboxylic acids in this study were converted to dicarboxylates, oxalic acid in **1a** exists as a monocarboxylate and adipic acid in **1i** remains intact. These differences are quite intriguing because such anomalies could not be explained with high degree of consistency and accuracy by mere structural considerations. Therefore, we looked at other physical properties, such as pK_a, which is the fundamental property that influences the conversion of an acid to a carboxylate. The analysis has provided vital information and a high correlation between pK_a and the observed structural variations.

pK_a towards specific host networks: The pK_a values for **1** and **1a–1i**, obtained from different references,[12] are listed in Table 1. By considering the ascending order of pK_a values, it is apparent that in this homologous series of dicar-

Table 1. pK_a values for **1** and aliphatic dicarboxylic acids in **1a–1i**.

Compound	Complex	pK_a	ΔpK_a
2,4-diamino-6-methyl-1,3,5-triazine		4.63	
oxalic acid	**1a**	1.23	3.40
acetylene dicarboxylic acid	**1e**	1.73	2.90
diglycolic acid	**1h**	2.79	1.84
malonic acid	**1b**	2.83	1.80
fumaric acid	**1d**	3.02	1.61
thiodiglycolic acid	**1g**	3.32	1.31
succinic acid	**1c**	4.19	0.44
glutaric acid	**1f**	4.33	0.30
adipic acid	**1i**	4.42	0.21

boxylic acids, acids with low pK_a values (oxalic: 1.23 and malonic: 2.83) took part in the creation of host network along with **1**. However, acids with a high pK_a value (succinic: 4.19, glutaric: 4.33, and adipic: 4.42) gave host–guest systems in which the acids remained as guests in the host network created by **1**. The other dicarboxylic acids (fumaric, acetylene dicarboxylic, thiodiglycolic, and diglycolic) also fall into one of these categories depending on their pK_a values. For example, the complexes of fumaric and thiodiglycolic acids (**1d** and **1g**), which have pK_a values of 3.02 and 3.32, respectively, formed complexes similar to **1c** and **1i**, whereas the complexes of acetylene dicarboxylic and diglycolic acids (**1e** and **1h**) formed complexes similar to **1a** and **1b**. Therefore, by taking into consideration the pK_a values of all the acids in this study, it is evident that acids with p$K_a < 3$ preferentially gave binary component hosts, whereas acids with p$K_a > 3$ directed the monohost assemblies. Although further microanalysis for the causes of such variations could not be established, this information perhaps would highlight the importance of physical and chemical properties of the co-crystallizing agents for the creation of desired supramolecular assemblies.

pK_a towards specific hydrogen bonding patterns: Another important anomaly in complexes **1a–1i** is the conversion of carboxylic acids to carboxylate moieties at random and as a result of this, different types of hydrogen-bonding patterns, that is, ionic or neutral, were formed. For example, both the −COOH groups were converted to dicarboxylates in **1b–1h**, which leads to the formation of ionic hydrogen bonds, such as N^+−H···O^-, N−H···O^-, and O−H···O^-, whereas only one of the −COOH groups converts to carboxylate in **1a** and both the −COOH groups remain intact in **1i**, and form O−H···N and N−H···O hydrogen bonds. It is thought that this transformation is an artifact of the strength of acidity and basicity features of the reactants in the complex, which can be accounted for by the pK_a values. Therefore, the difference in pK_a between the aza-donor compound and the acid should give an indication of proton transfer, which is ultimately related to the appearance of different types of hydrogen-bonding patterns in the structures. From Table 1, it is apparent that exact quantitative estimation could not be established, but a qualitative range of ΔpK_a value sheds some light on the process of proton transfer in complexes **1a–1i**. Thus, the −COOH groups in this study were found to be converted to carboxylates if the ΔpK_a value was >0.3; below this value, the −COOH groups remain intact (**1i**). Also, it is worth noting that deprotonation occurred for both −COOH groups in all complexes except **1a**. However, deprotonation of only one of the −COOH groups of oxalic acid in **1a** could be accounted for by the wide difference between pK_a1 (1.23) and pK_a2 (4.19), in contrast with other acids.

Conclusion

We have reported molecular adducts **1a–1i** produced by the crystallization of **1** with different aliphatic dicarboxylic acids, that is, oxalic, malonic, succinic, fumaric, acetylene dicarboxylic, glutaric, thiodiglycolic, diglycolic, and adipic acids. All complexes of **1** and the corresponding acid (2:1) were obtained from CH_3OH solution with the carboxylic acid groups converted to carboxylates, except in **1a** and **1i**. All the complexes serve as representative examples of host–guest assemblies, however, two types of host network were observed and the differences are attributed to variations in the pK_a values of the acid molecules under consideration. The prevailing host structure was composed only of molecules of **1** (**1c**, **1d**, **1f**, **1g**, and **1i**) when the pK_a of the acid was >3.0, whereas a host structure comprised of both **1** and the carboxylate was observed (**1a**, **1b**, **1e**, and **1h**) when the pK_a was <3.0. We believe that this direct relationship between the composition of the host networks and the pK_a value has not been established earlier and that this revelation may prompt an extensive study of many other acids and host–guest assemblies that may prove useful for the creation of selective host–guest structures for applications in diverse areas, such as catalysis[13] and separation processes.[14] In complexes **1a–1i**, the molecules of **1** in the host network exist either as triads (**1a**, **1b**, and **1e**) or dimers (**1c**, **1d**, **1f**–**1i**) that are exclusively formed by different types of N−H···N hydrogen bonds. In addition, we have noted that, except in the case of **1a** and **1i**, interactions between **1** and the corresponding acid molecules are ionic in nature, with proton transfer from the acid to **1**. In this regard, we have correlated these observations with the pK_a difference between **1** and the corresponding acids. These observations may also lead to the development of specific types of hydrogen-bonding patterns, such as ionic and neutral, by using different types of species. This could be useful for designing systems with a variety of physical properties, for example, solubility because it is dependent of the polarity of the substance with respect to the solvent. Herein, we have compiled an exhaustive and systematic study of the host–guest structures of **1** with different dicarboxylic acids that demonstrates the ability of triazine systems to produce supramolecular assemblies with a variety of exotic architectures with ease.

Experimental Section

Preparation of molecular adducts of molecular complexes, 1a–1i: All chemicals used in this study were obtained from commercial suppliers (Sigma-Aldrich) and were used without further purification. The spectroscopic grade solvents employed for the crystallization purpose were of the highest available purity. Molecular adducts were prepared by dissolving **1** and the corresponding dicarboxylic acid in a 1:1 ratio in CH_3OH and then slowly evaporating the obtained solution. Single crystals were obtained over a period of 48 h in all cases. In a typical preparation, compound **1** (0.0625 g, 0.5 mmol) and succinic acid (0.0590 g, 0.5 mmol) were dissolved in CH_3OH (20 mL) by gentle warming in a water bath. The resultant solution was evaporated under ambient conditions and with protection from external mechanical disturbances, and within 48 h, good

Table 2. Crystallographic data for the CH_3OH adduct of **1** and the molecular adducts **1a–1i.**

	1	**1a**	**1b**	**1c**	**1d**
formula	$C_4H_7N_5{\cdot}CH_3OH$	$C_4H_8N_5{\cdot}C_4H_7N_5{\cdot}C_2H_1O_4{\cdot}CH_3OH$	$2\,C_4H_8N_5{\cdot}1\,C_3H_2O_4{\cdot}4\,H_2O$	$2\,C_4H_8N_5{\cdot}1\,C_4H_4O_4$	$2\,C_4H_8N_5{\cdot}C_4H_2O_4$
M_r	157.19	372.37	426.42	368.38	366.36
crystal shape, color	blocks, colorless	blocks, colorless	rods, colorless	rectangular blocks, colorless	blocks, colorless
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$	*C*2/*c*	$P2_1/n$	$P2_1/n$
a [Å]	20.857(6)	7.170(3)	22.193(3)	5.390(1)	5.409(1)
b [Å]	5.409(2)	9.789(4)	4.598(1)	11.467(1)	11.634(2)[Å]
c [Å]	13.911(4)	12.329(5)	19.397(3)	13.629(1)	13.556(2)
α [°]	90	81.20(1)	90	90	90
β [°]	95.46(1)	79.76(1)	103.48(1)	100.08(1)	100.57(1)
γ [°]	90	72.53(1)	90	90	90
V [Å^3]	1562.3(9)	807.7(6)	1924.8(6)	829.4(2)	838.6(2)
Z	8	2	4	2	2
ρ_{calcd} [g cm^{-3}]	1.337	1.531	1.471	1.475	1.451
T [K]	133(2)	133(2)	273(2)	273(2)	298(2)
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.100	0.123	0.124	0.115	0.113
2θ range [°]	50.52	50.60	50.48	50.48	50.52
limiting indices	$-24\le h\le 22$ $-6\le k\le 4$ $-16\le l\le 15$	$-8\le h\le 8$ $-11\le k\le 11$ $-14\le l\le 14$	$-23\le h\le 26$ $-5\le k\le 5$ $-23\le l\le 12$	$-6\le h\le 6$ $-13\le k\le 13$ $-16\le l\le 8$	$-6\le h\le 6$ $-13\le k\le 13$ $-16\le l\le 16$
F(000)	672	392	904	388	384
obsd reflns	3778	8034	4616	4079	5953
unique reflns [*R*(*int*)]	1417	2943	1755	1505	1525
reflns used	921	2188	1361	1440	1295
no. of params	103	240	157	124	123
GOF on F^2	1.072	1.178	1.142	1.110	1.038
*R*1 [$I>2\sigma(I)$]	0.0854	0.0926	0.0736	0.0369	0.0408
*wR*2	0.1952	0.2063	0.1482	0.1025	0.1137
max/min residual peaks [e Å^{-3}]	0.382/−0.345	0.364/−0.385	0.268/−0.282	0.218/−0.198	0.180/−0.203

	1e	**1f**	**1g**	**1h**	**1i**
formula	$2\,C_4H_8N_5{\cdot}1\,C_4O_4{\cdot}1\,H_2O$	$2\,C_4H_8N_5{\cdot}1\,C_5H_6O_4$	$2\,C_4H_8N_5{\cdot}1\,C_4H_4O_4S_1$	$2\,C_4H_8N_5{\cdot}1\,C_4H_4O_5{\cdot}O$	$2\,C_4H_7N_5{\cdot}1\,C_6H_{10}O_4$
M_r	382.36	382.41	400.44	402.40	396.43
crystal shape, color	rectangular blocks, colorless	blocks, colorless	rods, colorless	rods, colorless	rods, colorless
crystal system	triclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$P\bar{1}$	$Pca2_1$	$Pca2_1$	F_{ddd}	$P2_1/c$
a [Å]	9.368(1)	30.431(6)	31.408(4)	10.734(2)	10.130(2)
b [Å]	9.909(1)	5.132(1)	4.938(1)	24.449(6)	7.558(1)
c [Å]	10.807(1)	11.515(2)	11.596(1)	27.871(6)	13.244(2)
α [°]	66.85(1)	90	90	90	90
β [°]	66.85(1)	90	90	90	90
γ [°]	63.14(1)	90	90	90	90
V [Å^3]	820.9(1)	1798.3(6)	1798.5(5)	7314(3)	954.6(3)
Z	2	4	4	16	2
ρ_{calcd} [g cm^{-3}]	1.547	1.412	1.479	1.454	1.379
T [K]	273(2)	298(2)	273(2)	273(2)	298(2)
λ ($Mo_{K\alpha}$) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.124	0.109	0.224	0.118	0.105
2θ range [°]	50.46	50.46	50.48	50.46	50.50
limiting indices	$-11\le h\le 11$ $-11\le k\le 11$ $-12\le l\le 12$	$-35\le h\le 36$ $-6\le k\le 6$ $-9\le l\le 13$	$-28\le h\le 37$ $-5\le k\le 5$ $-13\le l\le 13$	$-12\le h\le 10$ $-29\le k\le 25$ $-33\le l\le 30$	$-12\le h\le 10$ $-8\le k\le 9$ $-15\le l\le 15$
F(000)	400	808	840	3360	420
obsd reflns	6000	8181	8399	8805	4592
unique reflns [*R*(*int*)]	2940	1714	3220	1661	1706
reflns used	2603	1539	3078	1310	1492
no. of params	262	286	261	129	164
GOF on F^2	1.193	1.091	1.070	1.171	1.121
*R*1 [$I>2\sigma(I)$]	0.0582	0.0418	0.0353	0.0898	0.0461
*wR*2	0.1202	0.1005	0.0899	0.1838	0.1246
max/min residual peaks [e Å^{-3}]	0.309/−0.281	0.194/−0.162	0.274/−0.160	0.619/−0.273	0.241/−0.298

Table 3. Bond lengths, l [Å] and angles, $\measuredangle$ [°] of the hydrogen bonds observed in the CH_3OH adduct of **1** and also adducts **1a–1i.**

	1		**1a**		**1b**		**1c**		**1d**	
	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]
N–H···N	2.12, 2.98	173	2.10, 2.94	165	2.13, 2.99	176	2.20, 3.06	175	2.24, 3.10	175
	2.16, 3.01	175	2.18, 3.03	171	2.23, 3.02	153				
			2.19, 3.04	170						
			2.50, 3.36	176						
N–H···O	2.21, 3.05	164	2.06, 2.91	169	2.02, 2.83	157				
	2.24, 2.92	136								
N–H···O^-			1.88, 2.74	174	1.91, 2.77	175	1.99, 2.80	156	1.99, 2.80	157
			1.98, 2.75	149			2.05, 2.85	156	2.08, 2.94	173
			2.06, 2.91	166			2.06, 2.91	172	2.10, 2.91	158
N^+–H···O			1.87, 2.73	174						
N^+–H···O^-					1.80, 2.67	173	1.68, 2.64	174	1.78, 2.64	176
O–H···N	1.97, 2.79	172	1.83, 2.64	170						
O–H···O					1.83, 2.75	175				
					2.00, 2.91	162				
O–H···O^-			1.87, 2.59	147	1.88, 2.79	168				
					1.92, 2.76	165				
C–H···N							2.64, 3.55	156	2.68, 3.45	140
C–H···O^-							2.51, 3.42	159	2.58, 3.51	164

	1e		**1f**		**1g**		**1h**		**1i**	
	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]	l [Å]	$\measuredangle$ [°]
N–H···N	2.17, 3.03	178	2.10, 3.05	172	2.14, 3.00	176	2.16, 3.01	174	2.09, 3.00	176
	2.17, 3.03	178	2.12, 2.99	172	2.17, 3.03	176	2.24, 3.09	169		
	2.18, 3.04	172								
N–H···O	1.97, 2.74	148					2.20, 2.92	142	2.10, 2.93	173
									2.21, 3.07	174
									2.26, 3.08	156
N–H···O^-	1.99, 2.83	169	1.95, 2.80	170	1.99, 2.81	159	2.01, 2.86	171		
	2.10, 2.95	171	2.06, 2.91	160	2.02, 2.88	169				
	2.18, 2.81	130	2.07, 2.87	154	2.04, 2.88	155				
	2.28, 3.13	173	2.07, 2.88	152	2.07, 2.84	149				
	2.47, 3.15	137	2.11, 2.87	148	2.13, 2.94	156				
			2.34, 3.03	146	2.62, 3.35	144				
N^+–H···O^-	1.74, 2.67	165	1.72, 2.58	176	1.76, 2.62	176	1.76, 2.61	171		
	1.81, 2.71	176	1.80, 2.66	178	1.78, 2.64	176				
O–H···N									1.68, 2.65	171
O–H···O^-	1.88, 2.74	169								
	2.15, 2.88	143								
C–H···N									2.48, 3.29	141
C–H···O	2.54, 3.48	168								
C–H···O^-			2.43, 3.34	158	2.48, 3.35	150				
					2.49, 3.24	135				

quality, colorless crystals of **1c** were obtained that were suitable for single-crystal X-ray diffraction studies.

Crystal structure determination of 1a–1i: Good quality single crystals of **1a–1i**, and also the CH_3OH adduct of **1**, were obtained by the procedure described above, were chosen after being viewed under a microscope, glued to a glass fiber by using an adhesive, and mounted on the goniometer of Bruker single-crystal X-ray diffractometer equipped with an APEX CCD detector. In all cases, data collection was smooth and without any complications, and all the crystals were stable throughout the data collection period. The intensity data were processed by using the Bruker SAINT suite of programs,[15] followed by absorption correction with SADABS.[15] The structures were solved by using SHELXS and refined by least-square methods using SHELXL.[15] All nonhydrogen atoms were refined by anisotropical methods and hydrogen atoms were either refined or placed in calculated positions.

All the structural refinements converged to good R factors, as listed in Table 2, and the intermolecular interactions were computed by using PLATON software[16] and have been given in Table 3. The packing diagrams were generated by using Diamond version 3.1f.[17]

CCDC-668412–668421 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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