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Solid state structural study on recognition of aromatic dicarboxylic acids by substituted amino-pyrimidines and its supramolecular network

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Abstract

A series of co-crystals containing substituted 2-aminopyrimidines (2AP) with different dicarboxylic acids have been synthesized and their interactive modes have been characterized by single crystal X-ray studies. For this purpose three complexes containing 2-amino-4,6-dimethylpyrimidine and terephthalic acid (complex **1**), 2-amino-4-methyl-6-phenylpyrimidine and isophthalic acid (complex **2**), 2-amino-4,6-diphenylpyrimidine and terephthalic acid (complex **3**) have been synthesized. Substituents of the 2AP ring have been changed carefully from dimethyl, methyl–phenyl to diphenyl in increasing order of their size to study the change in their crystal engineering and overall supramolecular architecture.

Keywords: Molecular recognition; 2-Aminopyrimidine; Dicarboxylic acid; Supramolecular chemistry; Crystal engineering

1. Introduction

Crystal engineering [1] and supramolecular chemistry [2] is a rapidly expanding area of solid-state chemical research for its versatile applications in the field of molecular biology [3], materials science [4] and pharmaceutical science [5]. Supramolecular architecture is built up by different hydrogen bonding interactions as well as by various non-bonding weak interactions. Supramolecular hetero synthons have been formed initially by hydrogen bonding which further developed a whole network by different directional weak interactions [6].

Solid phase recognition of dicarboxylic acids [7] with varied designed or ready-made receptors is an enormously promising field in various artificial supramolecular architectures as well as in highly important synthetic materials. Receptors having pyridine amides are used for the recognition of a carboxylic acid group. Here one set of donor–acceptor is available to recognize only one carboxylic acid moiety. But if the receptor containing 2-aminopyrimidine (2AP) [8] is used for the recognition of carboxylic acid group, it has different modes of hydrogen bonding set to recognize both monocarboxylic [9] and dicarboxylic acids [10]. It also plays a great role in coordination as well as in metal containing supramolecular assemblies [11]. Each receptor containing 2AP moiety has two sets of donor–acceptor arrays (Fig. 1a) which may recognize either two carboxylic acid groups (Fig. 1b) or one set being involved for the recognition of one carboxylic acid and the other set being involved for the dimerization (Fig. 1c) with another molecule containing 2AP moiety [12]. In this work, we have disclosed the changes in supramolecular behavior of the complexes containing different dicarboxylic acids with differentially substituted 2AP. Here we have used

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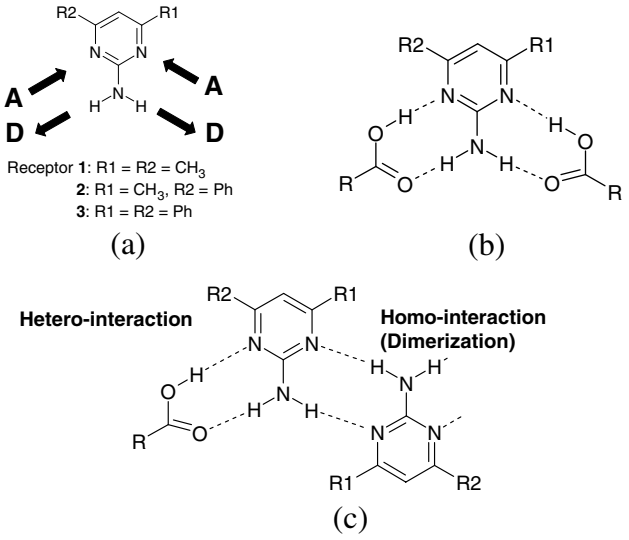

Fig. 1. Schematic representation of receptors containing 2-aminopyrimidine (2AP) moiety: (a) two sets of donor–acceptor arrays of the receptors; (b) hydrogen bonding pattern with two carboxylic acid groups; (c) hydrogen bonding pattern with carboxylic acid group and another 2AP moiety.

substituted 2AP which we have synthesized for this study [13]. For complex **1**, we have used 2-amino-4,6-dimethylpyrimidine and terepthalic acid. Complexes **2** and **3** have been synthesized from 2-amino-4-methyl-6-phenylpyrimidine, 2-amino-4,6-diphenylpyrimidine and isophthalic and terephthalic acids respectively. So in this progression, from dimethyl to diphenyl via methyl–phenyl, the supramolecular networks as well as the packing patterns in the solid state of the complexes change dramatically. By simply changing the substituents (alkyl/aryl) in the pyrimidine ring, the supramolecular arrays differ markedly from the planar one-dimensional wave like network to the three-dimensional complex polymeric network. Though the study of supramolecular behavior of simple 2-aminopyrimidine and some cases of substituted pyrimidines with different dicarboxylic acids have been reported, the changing architecture with varying substituents of different size is important in the context of crystal engineering.

2. Results

Details of the synthesis of the complexes, X-ray data collections and structure solutions/refinements are given in the experimental section. Crystallographic data and hydrogen bond metrics are summarized in Tables 1–4 with ORTEP diagrams shown in Fig. 2.

Table 2
Hydrogen-bond parameters (Å, °) of complex **1**

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1O1···N1^{i}	1.05	1.5750	2.6168(18)	172
N3–H1N3···O2^{ii}	0.91	1.9667	2.8768(18)	177
N3–H2N3···N2^{iii}	0.91	2.0919	3.0042(18)	176
C3–H3A···*Cg*1^{iv}	0.93	3.2857	3.3601(17)	87

Symmetry codes: (i) $-1+x, y, z$; (ii) $1+x, y, z$; (iii) $2-x, -1-y, -z$; (iv) $-1+x, y, z$; *Cg*1 is the centroid of the ring N1/C1/N2/C2/C3/C4.

Table 1
Crystallographic data and structure refinement parameters of complex **1**, complex **2** and complex **3**

Compound	Complex **1**	Complex **2**	Complex **3**
CCDC No.	638339	638340	638341
Empirical formula	$C_8H_6O_4,2(C_6H_9N_3)$	$C_8H_6O_4,2(C_{11}H_{11}N_3)$	$C_8H_6O_4,2(C_{16}H_{13}N_3)$
Formula weight	412.45	536.58	660.72
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
T [K]	100.0(1)	297(2)	100.0(1)
a [Å]	3.8923(1)	11.137(5)	9.4434(7)
b [Å]	15.1100(4)	10.596(5)	9.5540(7)
c [Å]	16.7463(4)	22.789(11)	10.0176(8)
α [deg]	90	90	104.577(1)
β [deg]	98.042(2)	96.864(8)	91.342(1)
γ [deg]	90	90	114.101(1)
Z	2	4	1
V [Å^3]	975.21(4)	2670(2)	790.28(10)
$\ddot{I}$ [Å]	0.71073	0.71073	0.71073
D_{calc} [mg/m^3]	1.405	1.335	1.388
F [000]	436	1128	346
μ [mm^{-1}]	0.101	0.091	0.092
2θ [°]	2.7–28.5	1.80–25.00	4.08–27.50
Index ranges	$-5 \leqslant h \leqslant 5$	$-13 \leqslant h \leqslant 12$	$-11 \leqslant h \leqslant 12$
	$-20 \leqslant k \leqslant 20$	$-11 \leqslant k \leqslant 12$	$-12 \leqslant k \leqslant 12$
	$-22 \leqslant l \leqslant 22$	$-26 \leqslant l \leqslant 25$	$-13 \leqslant l \leqslant 10$
Reflections collected	11495	5759	5402
Unique reflections	2468	2296	3476
Observed reflections	1822	1990	2963
R_1 [$I > 2\sigma(I)$]	0.0505	0.0857	0.0428
wR_2	0.1093	0.2128	0.1061
GOF	1.051	1.046	1.055