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Molecular Recognition Induced Supramolecular Array of 2-Aminopyrimidine with Terephthalic Acid, 1,4-Phenylenediacetic Acid and Fumaric Acid in Solid State *via* H-bonding and π-stacking Interactions*

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The crystal structures of molecular complexes of 2-aminopyrimidine (2AP) with terephthalic acid (1) (1 : 1; Complex A), 1,4-phenylenediacetic acid (2) (1 : 1; Complex B) and fumaric acid (3) (1 : 2; Complex C) were determined. Complex A is orthorhombic, space group Pnma, with $a = 13.0323(3)$, $b = 23.9443(1)$, $c = 3.7927(1)$ Å; $\alpha = \beta = \gamma = 90^\circ$; $Z = 4$; $D_{calc} = 1.466\,Mg/m^3$; final $R = 0.0384$, $wR^2 = 0.0939$ for 1381 independent reflections. Complex B is orthorhombic, space group Pbcn with $a = 4.5686(1)$, $b = 15.7687(2)$, $c = 20.1621(4)$ Å; $\alpha = \beta = \gamma = 90^\circ$; $Z = 4$; $D_{calc} = 1.323\,Mg/m^3$; final $R = 0.0461$, $wR^2 = 0.1158$ for 1662 independent reflections. Complex C is monoclinic, space group $P2_1/c$ with $a = 3.7946(2)$, $b = 19.1766(7)$, $c = 13.0641(6)$ Å; $\alpha = 90^\circ$, $\beta = 96.893(1)^\circ$, $\gamma = 90^\circ$; $Z = 4$; $D_{calc} = 1.486\,Mg/m^3$; final $R = 0.0665$, $wR^2 = 0.1626$ for 2752 independent reflections. 2AP generates supramolecular assembly with 2 and 3 *via* non-conventional weak C-H—O hydrogen bonding. Interestingly only in the case of Complex C, proton transfer occurs to the ring nitrogen of 2AP from 3. A novel hydrogen-bonding motif for the control of solid-state structures has been developed. The motif is based on the hydrogen bonding complementarity of dicarboxylic acids with 2AP.

Keywords: Molecular recognition, hydrogen bonding, π-stacking and molecular hetero-assembly

INTRODUCTION

Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable aggregates, joined by noncovalent bonds, with well defined composition and structure [1]. Careful choice of complementary binding groups will lead not only to strong but also discriminating interaction in the solid state. Most of the supramolecular crystals are originated from conventional, strong N-H—X and O-H—X (X = O,N) hydrogen bonds. The weak hydrogen bonds such as C-H—O [2] and C-H—N [3] are known to play a significant role in the determining the molecular packing of organic solids. In continuation

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of our research interest in molecular recognition studies on dicarboxylic acids [4], we report here the crystal structures of some interesting molecular complexes of 2AP with terephthalic acid, 1,4-phenylenediacetic acid and fumaric acid respectively.

2AP has two equivalent proton donors and two equivalent proton acceptors [5] available for hydrogen bonding with neighbouring molecules. Hetero-assembly with 2AP could be prepared by the addition of a dicarboxylic acid guest that forms preferentially hydrogen bonds with 2AP rather than forming self-assembled [6, 7] hydrogen bonds and they form cyclic hydrogen bonded dimers like 2AP [6]. The crystal structures of 2AP with succinic acid [8] and terephthalic acid [9] have been reported, but in both cases C-H—O hydrogen bondings were not observed to form a supramolecular hydrogen bonding array though succinic acid contains α-hydrogens. The goal of this co-crystal structural study was to investigate the ability of 2AP in the formation of different hydrogen bonding pattern with different dicarboxylic acids although the basic hydrogen bonding units are same.

RESULTS AND DISCUSSION

Complex A

Terephthalic acid typically associates with 2-aminopyrimidine by N-H—O and O-H—N hydrogen bonds through the formation of eight-membered hydrogen bonded rings (Fig. 1). The acid molecule (within ±0.028(1) Å) makes a dihedral angle of 22.34(6)° with the planar pyrimidine ring. These heterodimers form hydrogen-bonded zig-zag chains extended along [010] axis (Fig. 2).

The pyrimidine and benzene rings are stacked independently along [001] axis (Fig. 3) with N1-C2 $(x, y, z+1)$ 3.364 (2) Å being the shortest contacts for the pyrimidine rings and C5—C6 $(x, y, z+1)$ 3.513 (2) Å for the benzene rings respectively.

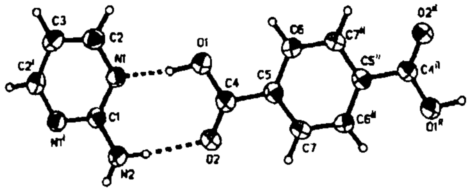

FIGURE 1 ORTEP diagram of complex A showing displacement ellipsoids at the 50% probability level.

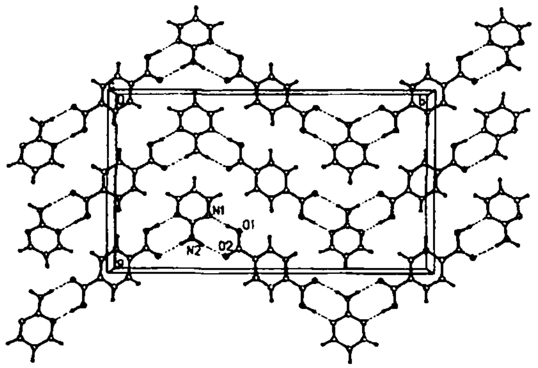

FIGURE 2 Hydrogen bonding network in crystal lattice of complex A.

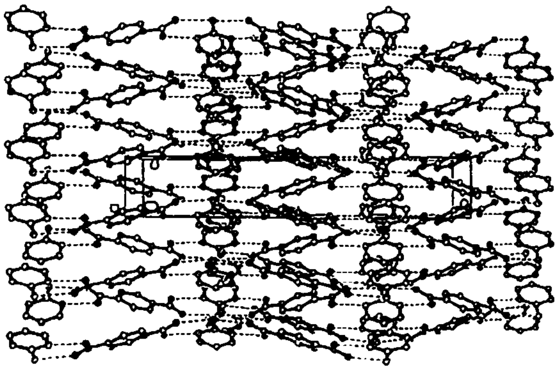

FIGURE 3 Supramolecular array of complex A showing stacking mode along (001) axis.

The bond lengths and bond angles observed in the molecules of the co-crystal agree with those observed in the independent crystal structures [10].

Complex B

The asymmetric unit contains one-half molecule for each 2-aminopyrimidine and 1,4-phenylenediacetic acid with other-half being symmetry related (Fig. 4). 2-Aminopyrimidine is related by a crystallographic two-fold axis passing through the atoms N2, C6 and C8 whereas 1,4-phenylenediacetic acid is inversion related. The carboxylic acid group (O1, O2, C4 and C5) makes a dihedral angle of 77.54(8)° with the phenyl ring.

The planar 2-aminopyrimidine molecule is linked to the 1,4-phenylenediacetic acid by N-H—O and O-H—N intermolecular hydrogen bonds (N2-H1N2 0.91(2), H1N2—O1 2.02(2), N2-O1 2.921(2)Å, N2-H1N2—O1 174(2)Å; O2-H1O2 1.04(3), H1O2—N1 1.65(3), O2—N1 2.676(2)Å, O2-H1O2—N1 172(2)Å. The donor and acceptor atoms in these hydrogen bonds along with C5 and C6 form a eight-membered ring which is coplanar with the pyrimidine moiety. Since these molecules lie across the crystallographic symmetry elements they form an infinite wave like chain in the solid state.

The chains translated one unit along [100] axis are linked by weak C-H—O contacts involving C4 and O1(C4-H4A 1.00(3), H4A—O1 2.56(3), C4A—O1 3.541(3)A, C4-H4A—O1 167(2)°. The pyrimidine and phenyl rings translated one unit along [100] axis are stacked (Fig. 5) with perpendicular distances of 3.605 and 3.614Å, respectively. The line joining the centroids of adjacent rings form angles of 37.91° and 37.72° respectively with the normal to the planes. Thus benzylic hydrogens of the acid molecule of one layer are linked to carboxylic carbonyl oxygen atoms of another layer through hydrogen bonds in the crystal sheet and thus results a three point fixation [11] of carboxylic acid motif in the complex.

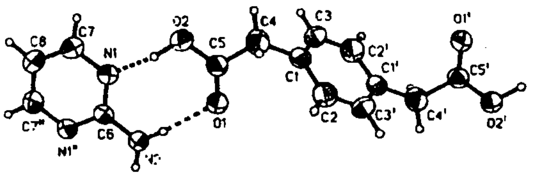

FIGURE 4 ORTEP diagram of complex B showing displacement ellipsoids at the 50% probability level.

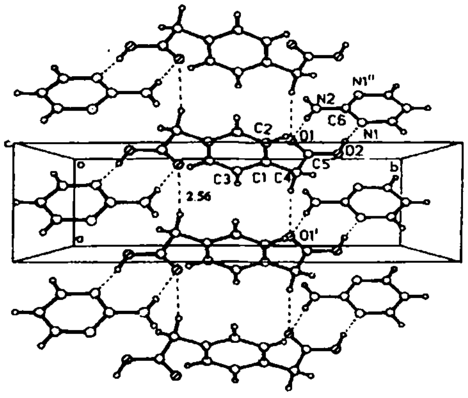

FIGURE 5 Interlayer Hydrogen bondings through C-H—O of complex B.

Complex C

The asymmetric unit contains a molecule of 2-aminopyrimidine and half molecule each of two fumaric acids (Fig. 6). The 2-amino pyrimidine is protonated at the N2 position which is transferred from one of the fumaric acid (all the hydrogen atoms were located from a difference Fourier map and no sign of any peak was seen near the O4 atom). Proton transfer is also corroborated from the ^{1}H NMR spectrum [12] (a broad signal appeared at δ 8.19 for ring N-H) of the complex crystal.

In complex C (Fig. 6), O4 makes two hydrogen bonds with N2-H (due to proton transfer from carboxylic group to ring N of 2AP) and O2-H of another formic acid molecule. Thus the charge density on O4 atom of carboxylate group is partially shared by these two hydrogen bonds showing the unequal bond distances in carboxylate group. The fumaric acid molecules form a dihedral angle of 12.51(8)° between them and they make dihedral angles of 27.66(9) and 16.74(9)° with the 2-aminopyrimidine.

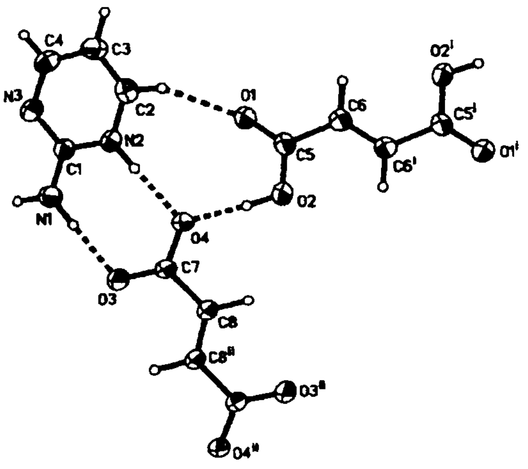

FIGURE 6 ORTEP diagram of complex C showing displacement ellipsoids at the 50% probability level.

The contents of the asymmetric unit are linked by two N-H—O, one O-H—O and one very weak C-H—O hydrogen bonds. In the solid state they extend along (010) axis to form an infinite plane wave like structure. The adjacent wave-like structures are linked by a network of N-H—O and weak C-H—O intermolecular hydrogen bonds to form a supramolecular structure (Fig. 7). The 2-amino pyridimine and both acid molecules translated along [100] axis are stacked (Fig. 8) as individual columns.

EXPERIMENTAL

General: Melting points were recorded (uncorrected) in open capillaries with a hot-stage apparatus (Toshniwal). IR spectra were recorded on a PERKIN-ELMER, MODEL No. 883, spectral bands are reported in cm^{-1}. Proton NMR (200 MHz) spectra were measured with a BRUKER AM-200 spectrometer; chemical shifts are expressed in ppm down field from internal Me$_4$Si. Elemental analysis was carried out in the Microanalytical Laboratory of Indian Association for the Cultivation of Science, Calcutta. Solvents were purified and dried in the usual manner before use.

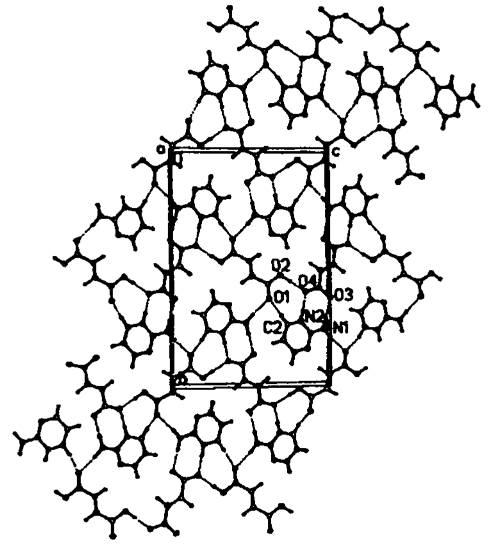

FIGURE 7 Hydrogen bonding network of Complex C.

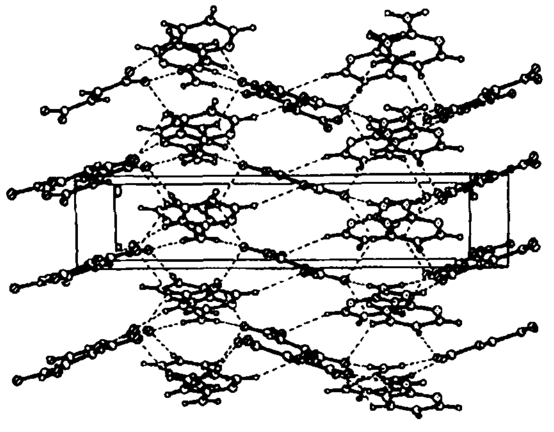

FIGURE 8 Column like stacked H-bonding network of Complex C.

Synthesis

Complex A

Single crystal was grown by slow evaporation of 5:1 mixture of a dry acetone and methanol solution of the 2-aminopyrimidine and terephthalic acid (1:1 mol. ratio). MP : 192°C. IR(KBr) cm^{-1}: 3369, 3322, 3199, 2436, 1672, 1289; ^{1}H NMR (200 MHz CDCl$_3$): δ8.27 (d, 2H, J = 6 Hz), 8.09 (bs, 4H), 6.59 (t, 1H, J =

6 Hz), 4.73 (bs, 2H, $-NH_2$); Anal. Calcd. for C12H11N3O4; C, 55.17; H, 4.24; N, 16.09%. Found: C, 55.18; H, 4.28; N, 16.14%.

Complex B

The complex B was prepared by mixing 2-aminopyrimidine with 1,4-phenylenediacetic acid (1 : 1) in dry acetone. The resulting solution was allowed to evaporate at rt to give the desired crystals, MP 154°C.

IR (KBr) cm^{-1}: 3384, 3332, 2455, 1904, 1695, 1566, 1341, 1243; ^1H NMR (200 MHz, $CDCl_3$): δ 8.19 (d, 2H, J = 6 Hz), 7.19 (s, 4H), 6.53 (t, 1H, J = 6 Hz), 5.49 (bs, 2H, $-NH_2$), 3.52 (s, 4H); Anal. Calcd. for C14H15N3O4: C, 58.13; H, 5.23; N, 14.53%. Found: C, 58.21; H, 5.32; N, 14.49%.

Complex C

The Complex C was grown by slow evaporation of 3:1 mixture of dry acetone and methanol solution of the 2-aminopyrimidine and fumaric acid (1:1 mol ratio). Colourless slab crystals of the complex appeared which was suitable for X-ray study. MP: 180 - 182°C.

IR (KBr) cm^{-1}: 3248, 2930, 1664, 1430, 1362, 1294, 1234; ^1H NMR (200 MHz $CDCl_3$): δ 8.19 [bs, 1H, (ring −NH)], 8.04 (d, 2H, J = 6 Hz), 6.56 (t, 2H, J = 6 Hz), 6.36 (d, 2H, J = 9.6 Hz), 4.71 (bs, 2H, $-NH_2$). Anal. Calcd. for C8H9N3O4: C, 45.50; H, 4.29; N, 19.89%. Found: C, 45.59; H, 4.27; N, 19.91%.

Experimental conditions are summarized in Table I. Positional and thermal parameters for non-hydrogen atoms are listed in Table II. Bond distances and bond angles are contained in Table III and the hydrogen bond data are listed in Table IV.

X-ray Structure Analysis

Data were collected on a SMART CCD area detector diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) with

TABLE I Crystal data and structure refinement for complex A, complex B and complex C

Complex	A	B	C
Empirical formula	C12H11N3O4	C14H15N3O4	C8H9N3O4
Formula weight	261.24	289.29	211.18
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pnma	Pbcn	$P2_1/c$
Unit cell dimensions (Å):			
a	13.0323 (3)	4.5686 (1)	3.7946 (2)
b	23.9443 (1)	15.7687 (2)	19.1766 (7)
c	3.7927 (1)	20.1621 (4)	13.0641 (6)
α	90°	90°	90°
β	90°	90°	96.893°
γ	90°	90°	90°
Volume ($Å^3$)	1183.51 (4)	1452.50 (5)	943.77 (7)
Z	4	4	4
Density (calculated)	1.466 Mg/m^3	1.323 Mg/m^3	1.486 Mg/m^3
Absorption coefficient (mm^{-1})	0.113	0.099	0.121
F(000)	544	608	440
Reflections collected	6833	8468	7257
Independent reflections	1381 [*R*(int) = 0.0280]	1662 [*R* (int) = 0.0287]	2752 [*R*(int) = 0.0417]
Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
Goodness-of-fit on F^2	1.073	1.078	1.055
Final *R* indices [$I > 2$ sigma(I)]	$R1 = 0.0384$, $wR^2 = 0.0939$	$R1 = 0.0461$, $wR^2 = 0.1158$	$R1 = 0.0665$, $wR^2 = 0.1626$
R indices (all data)	$R1 = 0.0532$, $wR^2 =$	$R1 = 0.0716$, $wR^2 = 0.1355$	$R1 = 0.1031$, $wR^2 = 0.1836$
Largest diff. peak and hole	0.175 and −0.140 $e.A^{-3}$	0.118 and −0.094 $e.A^{-3}$	0.387 and −0.227 $e.A^{-3}$

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic parameters ($A^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atoms	x	y	z	U(eq)
		Complex A		
O (1)	7904 (1)	3995 (1)	107 (4)	53 (1)
O (2)	9270 (1)	3576 (1)	2425 (4)	60 (1)
N (1)	6965 (1)	3000 (1)	88 (3)	37 (1)
N (2)	8256 (1)	2500	2775 (5)	41 (1)
C (1)	7382 (1)	2500	938 (5)	33 (1)
C (2)	6066 (1)	2988 (1)	– 1596 (4)	41 (1)
C (3)	5570 (2)	2500	– 2456 (6)	44 (1)
C (4)	8868 (1)	3983 (1)	1118 (4)	40 (1)
C (5)	9940 (1)	4514 (1)	523 (4)	36 (1)
C (6)	8965 (1)	4986 (1)	– 863 (4)	40 (1)
C (7)	10478 (1)	4531 (1)	1378 (4)	40 (1)
		Complex B		
O (1)	– 1401 (3)	6495 (1)	3543 (1)	96 (1)
O (2)	– 10 (3)	7763 (1)	3885 (1)	96 (1)
N (1)	– 3388 (3)	8492 (1)	2963 (1)	76 (1)
N (2)	– 5000	7247 (2)	2500	90 (1)
C (1)	970 (4)	5770 (1)	4733 (1)	69 (1)
C (2)	1813 (5)	5006 (1)	4470 (1)	89 (1)
C (3)	– 850 (5)	5751 (1)	5268 (1)	87 (1)
C (4)	1966 (5)	6603 (2)	4448 (1)	93 (1)
C (5)	16 (4)	6939 (1)	3912 (1)	72 (1)
C (6)	– 5000	8091 (2)	2500	68 (1)
C (7)	– 3460 (5)	9338 (1)	2954 (1)	87 (1)
C (8)	– 5000	9794 (2)	2500	93 (1)
		Complex C		
O (1)	1905 (6)	6291 (1)	6139 (1)	54 (1)
O (2)	801 (6)	5292 (1)	6887 (1)	55 (1)
O (3)	1719 (6)	6273 (1)	10140 (1)	53 (1)
O (4)	2351 (5)	6016 (1)	8517 (1)	47 (1)
N (1)	3200 (6)	7655 (1)	9664 (2)	42 (1)
N (2)	5257 (5)	7271 (1)	8169 (1)	33 (1)
N (3)	5203 (6)	8471 (1)	8576 (1)	40 (1)
C (1)	4566 (6)	7800 (1)	8804 (2)	31 (1)
C (2)	6686 (6)	7399 (1)	7289 (2)	37 (1)
C (3)	7389 (7)	8069 (1)	7026 (2)	42 (1)
C (4)	6561 (7)	8588 (1)	7704 (2)	43 (1)
C (5)	1165 (6)	5678 (1)	6083 (2)	36 (1)
C (6)	602 (7)	5319 (1)	5063 (2)	38 (1)
C (7)	1541 (6)	5858 (1)	9415 (2)	34 (1)
C (8)	346 (6)	5125 (1)	9556 (2)	37 (1)

a detector distance of 4 cm and swing angle of – 35°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different angle (0, 88, 180°) and each exposure of 10 s covered 0.3° in ω. The collected data were reduced by using the program SAINT [G.M. Sheldrick SAINT v4 Software Reference Manual, Siemens Analytical X-ray systems, Inc., Madison, Wisconsin, USA (1996)] and for reflections with $2\theta \leq 55°$ were used for further processing. The structure was solved by direct methods and refined by least-squares on F^2_{obs} by using the SHELXTL [G.M. Sheldrick, SHELXTL v5 Reference Manual, Siemens Analytical X-ray System, Inc., Madison, Wisconsin, USA (1996)] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference

TABLE III Selected bond lengths (Å) and angles (deg)

Complex A	
O(1)-C(4)	1.314 (2)
O(2)-C(4)	1.211 (2)
N(1)-C(2)	1.334 (2)
N(1)-C(1)	1.354 (14)
N(2)-C(1)	1.335 (3)
C(1)-N(1) #1	1.354 (14)
C(2)-C(3)	1.375 (2)
C(3)-C(2) #1	1.375 (2)
C(4)-C(5)	1.491 (2)
C(5)-C(7)	1.392 (2)
C(5)-C(6)	1.393 (2)
C(6)-C(7) #2	1.378 (2)
C(7)-C(6) #2	1.378 (2)
C(2)-N(1)-C(1)	116.65 (13)
N(2)-C(1)-N(1) #1	117.85 (9)
N(2)-C(1)-N(1)	117.85 (9)
N(1) #1-C(1)-N(1)	124.3 (2)
N(1)-C(2)-C(3)	122.9 (2)
C(2)-C(3)-C(2) #1	116.5 (2)
O(2)-C(4)-O(1)	123.50 (14)
O(2)-C(4)-C(5)	122.00 (13)
O(1)-C(4)-C(5)	114.50 (13)
C(7)-C(5)-C(6)	119.65 (13)
C(7)-C(5)-C(4)	118.48 (13)
C(6)-C(5)-C(4)	121.87 (13)
C(7) #2-C(6)-C(5)	120.07 (14)
C(6) #2-C(7)-C(5)	120.28 (13)
Complex B	
O(1)-C(5)	1.208 (2)
O(2)-C(5)	1.300 (2)
N(1)-C(7)	1.335 (2)
N(1)-C(6)	1.347 (2)
N(2)-C(6)	1.332 (3)
C(1)-C(3)	1.362 (3)
C(1)-C(2)	1.373 (3)
C(1)-C(4)	1.503 (3)
C(2)-C(3) #3	1.378 (3)
C(3)-C(2) #3	1.378 (3)
C(4)-C(5)	1.498 (3)
C(6)-N(1) #4	1.347 (2)
C(7)-N(1)-C(6)	116.5 (2)
C(3)-C(1)-C(2)	117.3 (2)
C(3)-C(1)-C(4)	120.5 (2)
C(2)-C(1)-C(4)	122.3 (2)
C(1)-C(2)-C(3) #3	121.5 (2)
C(1)-C(3)-C(2) #3	121.3 (2)
C(5)-C(4)-C(1)	113.9 (2)
O(1)-C(5)-O(2)	123.2 (2)
O(1)-C(5)-C(4)	123.8 (2)
O(2)-C(5)-C(4)	112.9 (2)
N(2)-C(6)-N(1)	117.99 (11)
N(2)-C(6)-N(1) #4	117.99 (11)
N(1)-C(6)-N(1) #4	124.0 (2)
N(1)-C(7)-C(8)	123.4 (2)
C(7) #4-C(8)-C(7)	116.2 (3)
Complex C	
O(1)-C(5)	1.209 (3)
O(2)-C(5)	1.306 (3)
O(2)-H1O2	0.92 (3)
O(3)-C(7)	1.233 (2)
O(4)-C(7)	1.284 (2)
N(1)-C(1)	1.322 (3)
N(1)-H1N1	0.96 (3)
N(1)-H2N1	0.95 (3)
N(2)-C(2)	1.352 (3)
N(2)-C(1)	1.355 (3)
N(2)-H1N2	0.91 (3)
N(3)-C(4)	1.324 (3)
N(3)-C(1)	1.349 (3)
C(2)-C(3)	1.364 (3)
C(2)-H(2)	0.96 (3)
C(3)-C(4)	1.394 (3)
C(3)-H(3)	0.96 (3)
C(4)-H(4)	0.97 (3)
C(5)-C(6)	1.491 (3)
C(6)-C(6) #3	1.310 (4)
C(6)-H(6)	1.02 (3)
C(7)-C(8)	1.494 (3)
C(8)-C(8) #5	1.311 (4)
C(8)-H(8)	1.03 (3)
C(5)-O(2)-H1O2	111.0 (18)
C(1)-N(1)-H1N1	118.6 (18)
C(1)-N(1)-H2N1	118.4 (16)
H1N1-N(1)-H2N1	123 (2)
C(2)-N(2)-C(1)	120.79 (18)
C(2)-N(2)-H1N2	119.9 (18)
C(1)-N(2)-H1N2	119.0 (18)
C(4)-N(3)-C(1)	116.82 (19)
N(1)-C(1)-N(3)	119.15 (19)
N(1)-C(1)-N(2)	119.20 (18)
N(3)-C(1)-N(2)	121.65 (18)
N(2)-C(2)-C(3)	119.8 (2)
N(2)-C(2)-H(2)	114.1 (15)
C(3)-C(2)-H(2)	126.1 (15)
C(2)-C(3)-C(4)	116.5 (2)
C(2)-C(3)-H(3)	121.9 (18)
C(4)-C(3)-H(3)	121.6 (18)
N(3)-C(4)-C(3)	124.5 (2)
N(3)-C(4)-H(4)	114.8 (16)
C(3)-C(4)-H(4)	120.7 (16)
O(1)-C(5)-O(2)	123.2 (2)
O(1)-C(5)-C(6)	120.69 (19)
O(2)-C(5)-C(6)	116.07 (19)
C(6) #3-C(6)-C(5)	123.6 (3)
C(6) #3-C(6)-H(6)	119.2 (15)
C(5)-C(6)-H(6)	117.1 (15)
O(3)-C(7)-O(4)	123.51 (19)
O(3)-C(7)-C(8)	120.06 (17)
O(4)-C(7)-C(8)	116.43 (17)
C(8) #5-C(8)-C(7)	123.4 (2)
C(8) #5-C(8)-H(8)	118.1 (18)
C(7)-C(8)-H(8)	118.5 (18)

Symmetry transformations: #1 $x, -y+1/2, z$ #2, $-x+2, -y+1, -z$ #3 $-x, -y+1, -z+1$ #4 $x-1, -y, z+1/2$ #5 $-x, -y+1, -z+2$.

synthesis and refined isotropically. Final conventional $R(F)$ and $wR(F^2)$ for observed reflections $[I > 2\sigma(I)]$ with weighting scheme, $w = 1/[\sigma^2(F_0^2) + (0.0534P)^2 + 0.2173P]$, where

TABLE IV Hydrogen bond parameters (Å,°)

	Complex A		
D-H—A	H—A	D—A	D-H—A
N2-H1N2—O2	2.02 (2)	2.89 (1)	166 (2)
O1-H1O1—N1	1.69 (3)	2.68 (2)	169 (2)
	Complex B		
D-H—A	H—A	D—A	D-H—A
O2-H1O2—N1	1.65 (2)	2.68 (2)	171.5 (2)
N2-H1N2—O1	2.02 (2)	2.92 (2)	173.8 (2)
C3-H3—O2	2.59 (2)	3.46 (3)	153.9 (2)
C4-H4A—O1	2.56 (2)	3.54 (3)	166. 7 (2)
	Complex C		
D-H—A	H—A	D—A	D-H—A
N1-H1N1—O3	1.84 (3)	2.79 (3)	176 (3)
N2-H1N2—O4	1.80 (3)	2.71 (2)	170 (3)
O2-H1O2—O4	1.63 (3)	2.55 (2)	172 (3)
C2-H2—O1	2.48 (3)	3.06 (3)	119 (2)
C2-H2—O1 #1	2.56 (3)	3.31 (3)	143 (2)
N1-H2N1—O1 #2	1.93 (3)	2.88 (3)	174 (2)
C4-H4—O2 #3	2.58 (3)	3.44 (3)	149 (2)
C3-H3—O3 #4	2.43 (3)	3.37 (3)	162 (2)

Symmetry transformations: #1 $x+1, y, z$; #2 $x, -y+3/2, z+1/2$; #3 $-x+1, y+1/2, -z+3/2$; #4 $x+1, -y+3/2, z-1/2$.

$P = (F_0^2 + 2F_c^2)/3$. The molecular graphics were done using SHELXTL.

CONCLUSIONS

This article thus demonstrates the role of 2AP in the formation of supramolecular structure with various dicarboxylic acids by utilising weak forces like hydrogen bonding, π-stacking *etc.*, and also shows how 2AP can be used to probe the hydrogen-bond preferences of carboxylic acid. All the crystal structures reported here involve a wave like or zig-zag pattern except the case of fumaric acid. In case of complex B and complex C, 1,4-phenylenediacetic acid and fumaric acid take part in unconventional C-H—O hydrogen bonding [$C(sp^3)$-H—O and $C(sp)^2$-H—O for complex B and C respectively] along with pyrimidine-pyrimidine (3.605 Å) and phenyl-phenyl (3.614 Å) stacking. This results an infinite wave like chain structures in the solid state. Most interestingly in complex C fumaric acid is complexed with 2AP *via* the formation of fused eight-nine membered hydrogen-bonded rings after the transfer of one proton to the pyrimidine ring nitrogen and ultimately forms a plane wave like structure. This is in contrast to succinic acid although it has the same geometrical orientation with succinic acid. All these supramolecular structures therefore demonstrate that acidity of the carboxylic acid as well as acidity of C-H proton of methylene or aromatic ring, govern the pattern of supramolecular structure in the solid state. Also in the solid state design, besides the arrays of conventional hydrogen bonds, C-H—O contacts play a significant role in futher modification of the structure of supramolecular assemblies.

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[12] All ^1H NMR, IR, Analysis and M.P. were noted by taking co-crystal of the corresponding complex.