

Structural and supramolecular insights into crystalline multicomponent systems of 2,4-diamino-6-phenyl-1,3,5-triazine with various carboxylic acids

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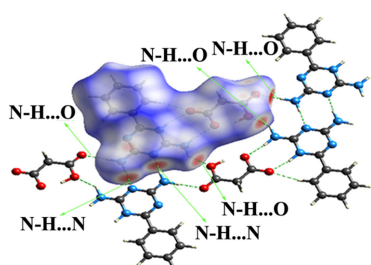
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Three multicomponent systems, namely, 2,4-diamino-6-phenyl-1,3,5-triazine–nicotinic acid (DAPT–NA), $C_9H_9N_5 \cdot C_6H_5NO_2$, (I), 2,4-diamino-6-phenyl-1,3,5-triazine-1-ium hydrogen malonate (DAPT–MMA), $C_9H_{10}N_5^+ \cdot C_3H_3O_4^-$, (II), and 2,4-diamino-6-phenyl-1,3,5-triazine-1-ium hydrogen (+)-dibenzoyl-D-tartrate (DAPT–DBTA), $C_9H_{10}N_5^+ \cdot C_{18}H_{13}O_8^-$, (III), have been synthesized and characterized *via* single-crystal X-ray diffraction, and their supramolecular interactions have been analysed. The formation of cocrystal (I) and salts (II) and (III) was confirmed through the widening of the C–N–C bond angle of the triazine moiety of 2,4-diamino-6-phenyl-1,3,5-triazine and the difference in the C–O bond distances between the carboxyl and carboxylate groups of the respective carboxylic acids. Cocrystal (I) and salt (II) form robust homomeric and heteromeric $R_2^2(8)$ ring motifs through primary acid–base interactions and complementary base pairing. In cocrystal (I), the complementary base pair exists as wave-like supramolecular strands, whereas in salt (II), it exists as a discrete pair. Salt (II) exhibits *DDDAAD* sextuple and *DADA* quadruple hydrogen-bonded arrays (*D* is donor and *A* is acceptor) through acid–base interactions and generates a supramolecular rosette-like architecture. In salt (III), the presence of carboxyl–carboxylate interactions and acid–base interactions led to the development of a supramolecular sheet and tunnel-like architecture. Cocrystal (I) and salt (III) are stabilized through offset aromatic π – π stacking interactions and C–H... π interactions, and salts (II) and (III) are stabilized *via* weak carbonyl– π and C–H...O hydrogen bonds. Macrocyclic $R_{12}^{12}(64)$ and $R_3^3(24)$ motifs are present in salts (II) and (III), respectively. Hirshfeld surface analysis of (I)–(III) reinforces the fact that N...H/H...N, O...H/H...O and C...H/H...C interactions contribute to the crystal packing and stability.

1. Introduction

The interplay of noncovalent interactions in supramolecular chemistry and molecular biology supports essential processes like DNA–protein binding, ion transport and enzyme catalysis (Lehn, 1988). Among the noncovalent interactions, hydrogen bonds are vital in enzymatic catalysis and metalloproteins, stabilizing metal–oxygen intermediates and enhancing selectivity in systems such as porphyrins (Mometeau *et al.*, 1994). In addition to hydrogen bonding, π – π stacking and C–H... π interactions significantly influence protein stability, folding and molecular recognition, particularly in structural element and self-assembly processes (Meyer *et al.*, 2003; Tewari & Dubey, 2008). Additionally, cation– π interactions play a key



role in stabilizing protein structures by positioning aromatic side chains and supporting α -helices and β -sheets (Minoux *et al.*, 1999).

2,4-Diamino-6-phenyl-1,3,5-triazine (DAPT) possesses a six-membered triazine core with amino substituents at the 2- and 4-positions and an arene group at the 6-position (Díaz-Ortiz *et al.*, 2004), facilitating both hydrogen-bonding and π - π stacking interactions. Nicotinic acid (NA) features a six-membered pyridine ring with a carboxyl group at the 3-position (Wright & King, 1953), enabling strong noncovalent interactions. Malonic acid (MA) consists of a three-carbon chain bearing terminal carboxyl groups (Goedkoop & MacGillavry, 1957) that increase its acidity and capacity for metal chelation. (+)-Dibenzoyl-D-tartaric acid (DBTA) contains esterified hydroxyl groups and benzoyl moieties that promote π - π stacking and hydrogen bonding. Collectively, these functional groups contribute to a diverse array of noncovalent interactions, significantly influencing the physicochemical properties of substances derived from them.

The type of noncovalent interactions present in a system alters the activity of DAPT when it interacts with biological target molecules (Nozaki *et al.*, 2004). The amino group of DAPT forms hydrogen bonds with the enzymes, stabilizing the DAPT-enzyme complex (Dai *et al.*, 2023). The arene group of DAPT stacks over the aromatic ring present in the amino acids in the enzymes to enhance the binding affinity and specificity. The presence of a ring N atom (Sütay *et al.*, 2012) results in strong electrostatic interactions with the charged residues of the enzymes of the microbes, increasing the specificity of the pharmaceutical action of DAPT.

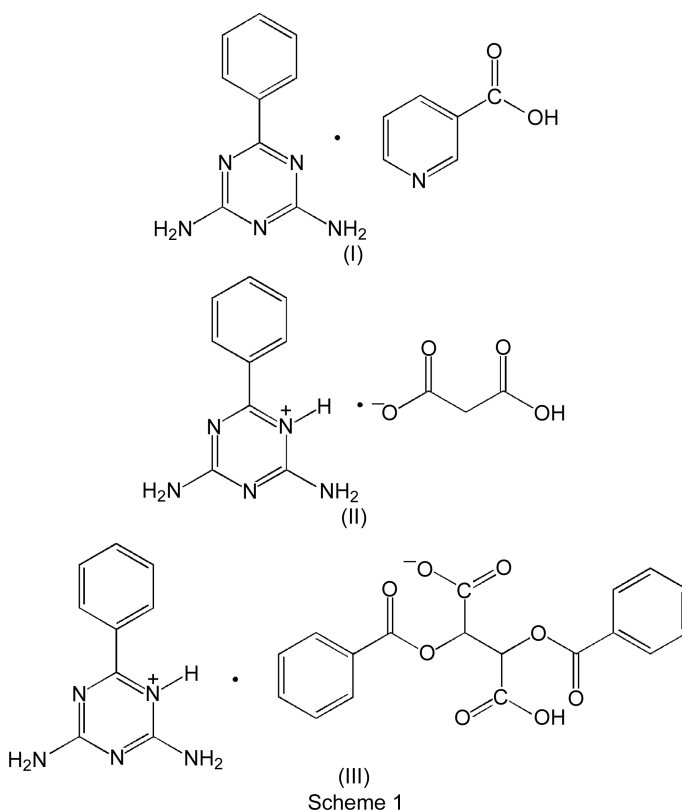
DAPT derivatives exhibit a broad spectrum of physiological properties, including antibacterial activities (Lebreton *et al.*, 2003; Srinivas *et al.*, 2006), by interacting with the synthesis of DNA and proteins in microbes, and anticancer activities (Hirose *et al.*, 1996; Ono *et al.*, 1996; Sato *et al.*, 1993; Sugie *et al.*, 1998), by disrupting the enzymes of cancer cells that are involved in nucleotide synthesis. In addition, 2,4-diamino-1,3,5-triazine derivatives are known for their anticancer (Sączewski *et al.*, 2006) and cardiotoxic activities (Kosary *et al.*, 1989). Furthermore, 1,3,5-triazine-substituted polyamines show potent antitrypanosomal activity against *Trypanosoma brucei* species, the causative agent of African sleeping sickness (Bacchi *et al.*, 1998; Kaminsky *et al.*, 1998; Klenke *et al.*, 2001). Triazine compounds also exhibit diverse therapeutic activities, including antiretroviral (Ludovici *et al.*, 2001), antidiabetic (Mylari *et al.*, 2003), antimalarial (Agarwal *et al.*, 2005) and antagonist (Mattson *et al.*, 2004) effects.

The formation of multicomponent systems *via* the approach of crystal engineering has been found to have a considerable impact on increasing the physicochemical activities of a drug, such as its solubility, bioavailability, thermal stability, photosensitivity, dissolution rate and selectivity, in a desired and controlled manner (Kumar *et al.*, 2017).

Numerous structural and supramolecular studies have demonstrated the application of organic/inorganic salts and cocrystals of DAPT through crystal engineering in pharmaceuticals. Mono/dicarboxylic acids have an exceptional ability

to form self-assemblies and bind easily with DAPT, resulting in the development of robust hydrogen-bonding patterns of great interest (Delori *et al.*, 2013; Goel *et al.*, 2013; Jali & Baruah, 2013; Wang *et al.*, 2014; Zheng *et al.*, 2018).

The current investigation aims to screen the various types of noncovalent interactions and supramolecular ring motifs that are exhibited by the multicomponent systems of DAPT with the carboxylic acids NA, MA and DBTA, namely, DAPT-NA, (I), DAPT-MA, (II), and DAPT-DBTA, (III) (see Scheme 1).



2. Experimental

2.1. Synthesis and crystallization

Compounds (I)–(III) were synthesized by mixing a hot alcoholic solution of 2,4-diamino-6-phenyl-1,3,5-triazine (DAPT) and nicotinic acid (methanol)/malonic acid (ethanol–water, 1:1 v/v)/(+)-dibenzoyl-D-tartaric acid (ethanol) in a 1:1 molar ratio and warming over a water bath for 20 min at 60 °C. The resulting solutions were then allowed to cool slowly and were kept for crystallization. After one week, colourless single crystals of (I)–(III) had formed and were harvested from their respective mother solutions.

2.2. Single-crystal X-ray diffraction data collection

The intensity data for (I)–(III) were collected on a Bruker D8 Venture Bio PHOTON III CMOS area-detector diffractometer with an Mo $K\alpha$ 1 μ S DIAMOND source (50 kV, 1.4 mA) at 173 K. The collection method involved ω - and φ -scans, and 1536 $\times$ 1024 bit data frames. The preliminary and full data sets were collected *via* APEX4 (Bruker, 2021).

Table 1
Experimental details.

Experiments were carried out at 173 K with Mo $K\alpha$ radiation using a Bruker APEX IV CCD diffractometer. H atoms were treated by a mixture of independent and constrained refinement.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_9H_9N_5 \cdot C_6H_5NO_2$	$C_9H_{10}N_5^+ \cdot C_3H_3O_4^-$	$C_9H_{10}N_5^+ \cdot C_{18}H_{13}O_8^-$
M_r	310.32	291.27	545.50
Crystal system, space group	Monoclinic, Pn	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$
a, b, c (Å)	9.2901 (9), 7.2116 (8), 11.5857 (12)	8.3350 (8), 5.1168 (4), 29.100 (2)	11.2689 (6), 7.6863 (3), 15.0741 (7)
β (°)	111.016 (4)	93.188 (3)	100.194 (2)
V (Å ³)	724.57 (13)	1239.15 (18)	1285.05 (10)
Z	2	4	2
μ (mm ⁻¹)	0.10	0.12	0.11
Crystal size (mm)	0.14 × 0.11 × 0.06	0.16 × 0.11 × 0.06	0.24 × 0.16 × 0.13
Data collection			
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11335, 2549, 2244	24363, 2183, 1895	22302, 4512, 4282
R_{int}	0.056	0.077	0.055
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.595	0.595	0.595
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.174, 1.09	0.037, 0.103, 1.06	0.031, 0.077, 1.09
No. of reflections	2549	2183	4512
No. of parameters	228	214	385
No. of restraints	9	7	8
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.49, -0.25	0.22, -0.29	0.12, -0.22
Absolute structure	Flack (1983)	—	Flack (1983)
Absolute structure parameter	0.500	—	0.500

Computer programs: *APEX4* (Bruker, 2021), *SAINT* (Bruker, 2021), *SHELXT2018* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020), *POVRay* (Cason, 2004), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

SAINT was used to integrate the data and *SADABS* was used to make empirical absorption corrections and scale the data. Space-group assignments were made *via XPREP* for all three compounds. Non-H atoms were first refined isotropically, followed by anisotropic refinement *via* full-matrix least-squares calculations based on F^2 . Using *WinGX* (Farrugia, 2012), the crystal structures were solved with the *SHELXT* (Sheldrick, 2015a) structure solution program *via* intrinsic phasing and refined with the *SHELXL* (Sheldrick, 2015b) refinement package *via* least-squares minimization.

2.3. Hirshfeld surfaces (HS) and fingerprint plots

The 3D HS analysis (Hirshfeld, 1977) (d_{norm} , shape index, curvedness and fragment patch) and 2D fingerprint plots (McKinnon *et al.*, 2007; Spackman & McKinnon, 2002) for (I)–(III) were performed and created using *CrystalExplorer17.5* (Turner *et al.*, 2017). This analysis provides a deeper insight into the intermolecular interactions within the crystals. The HS study maps intermolecular interactions in a crystal *via* atomic electron density. The molecular fingerprint, a 2D map derived from the HS, highlights the types and proportions of intermolecular interactions present.

2.4. Refinement

The crystal data for (I)–(III) are summarized in Table 1. H atoms bonded to N and O atoms were located from difference Fourier maps. The –NH hydrogen was refined freely and the –NH₂ and –OH hydrogens were refined with distances of

0.88 (2) and 0.84 (1) Å, respectively. Other H atoms were placed geometrically and refined *via* a riding model.

3. Results and discussion

3.1. Crystal structures

In the present work, the crystal structures and packing patterns of three distinct multicomponent systems (I)–(III) (Scheme 1) involving 2,4-diamino-6-phenyl-1,3,5-triazine (DAPT) and acids [nicotinic acid (NA), malonic acid (MA) and (+)-dibenzoyl-D-tartaric acid (DBTA)] have been discussed. The molecular structures of (I)–(III) are shown in Figs. 1(a)–(c). The cocrystal 2,4-diamino-6-phenyl-1,3,5-triazine–nicotinic acid (DAPT–NA), (I), features an asymmetric unit composed of one DAPT molecule and one NA molecule in a 1:1 ratio, as shown in Fig. 1(a). 2,4-Diamino-6-phenyl-1,3,5-triazine-1-ium hydrogen malonate (DAPT–MMA), (II), exists as a salt with its asymmetric unit comprising one DAPT cation and one hydrogen malonate (MMA) anion [Fig. 1(b)]. The asymmetric unit of 2,4-diamino-6-phenyl-1,3,5-triazine-1-ium hydrogen (+)-dibenzoyl-D-tartarate (DAPT–DBTA), (III), consists of one DAPT cation and one hydrogen (+)-dibenzoyl-D-tartarate (DBTA) anion [Fig. 1(c)].

The differences among (I)–(III) arise from the presence and absence of protonation of the ring N atom of DAPT. Compound (I) is a cocrystal, where there is no proton transfer from the acid group of NA. This is confirmed by the C–O bond lengths [C18–O1 = 1.232 (7) Å and C18–O2 = 1.293 (7) Å] (see Table S1 of the supporting information). The

formation of the cocrystal is also supported by the difference in bond lengths between the C—O groups (0.061 Å) of the carboxyl group of NA (Mekala *et al.*, 2018). Compounds (II) and (III) are salts, in which the protonation of DAPT occurs at the ring N1 position, which is evident from a slight increase in the C2—N1—C6 bond angles [119.04 (12) and 118.9 (2)°; see Tables S2 and S3 of the supporting information], whereas this angle is 118.6 (4) for cocrystal (I). The other two ring N atoms (N3 and N5) remain unprotonated in both salts (Caimac *et al.*, 2021; Sangeetha *et al.*, 2018; Sundaramoorthy *et al.*, 2014). Among the two carboxyl groups in MMA [in (II)] and DBTA [in (III)], one exists as the carboxylate ion and the other remains as a carboxyl group, which is evident from the $\Delta D(C-O)$ values (0.0316, 0.009, 0.0983 and 0.073 Å, respectively). These values agree with those observed for salts (<0.03 Å) and cocrystals (>0.08 Å) in the literature (Mekala *et al.*, 2018).

In (I)–(III), the ring N atoms (N1, N3 and N5) and the amino N atoms (N2 and N4) of DAPT, as well as the ring N atom (N6) of NA, are sp^2 -hybridized, as indicated by their respective bond angles being closer to 120°. The dihedral angles between the 2,4-diamino-1,3,5-triazine moiety and the arene group of DAPT in (I)–(III) are 16.6 (3), 3.84 (6) and 21.66 (12)°, respectively, which indicate that both rings are nearly coplanar to relieve steric interactions. The dihedral angles between the plane of DAPT and the plane of NA in (I),

MMA in (II) and DBTA in (III) are 2.92 (16), 5.90 (4) and 20.11 (5)°, respectively, which presumably reveals that the near coplanarity in cocrystal (I) enhances strong interactions and tight crystal packing, whereas salt (II) shows a slight deviation and slightly weaker interactions compared to (I), and that in salt (III) is significantly twisted, leading to weaker interactions. In salt (III), the DBTA ion has a (2*S*,3*S*) configuration (Mravik *et al.*, 1996). The torsion angles C13—C14—C15—C16, O2—C13—C14—O5, O1—C13—C14—O5, O7—C15—C16—O3 and O7—C15—C16—O4 of the DBTA ion are 168.02 (18), −176.04 (18), 4.8 (3), 164.8 (2) and −17.4 (3)°, respectively. The torsion angles of −176.04 (18) and 164.8 (2)° suggest stable antiperiplanar conformations (Rychlewska & Warzajtis, 2001), minimizing steric hindrance, and the torsion angles 4.8 (3) and −17.4 (3)° suggest less stable synperiplanar conformations due to increased steric interactions. These angles suggest that the molecule adopts conformations to balance stability, with some parts being more staggered (antiperiplanar) and others being more eclipsed (synperiplanar). The torsion angle of 168.02 (18)° for the carbon skeleton of DBTA indicates a near-antiperiplanar conformation, which contributes to the overall stability of the molecule. The torsion angle O7—C15—C14—O5 between the two benzoyl groups of the DBTA ion is 53.1 (2)°, which indicates a *gauche* conformation for the groups. The dihedral angle between C(H)(OCOPh)-

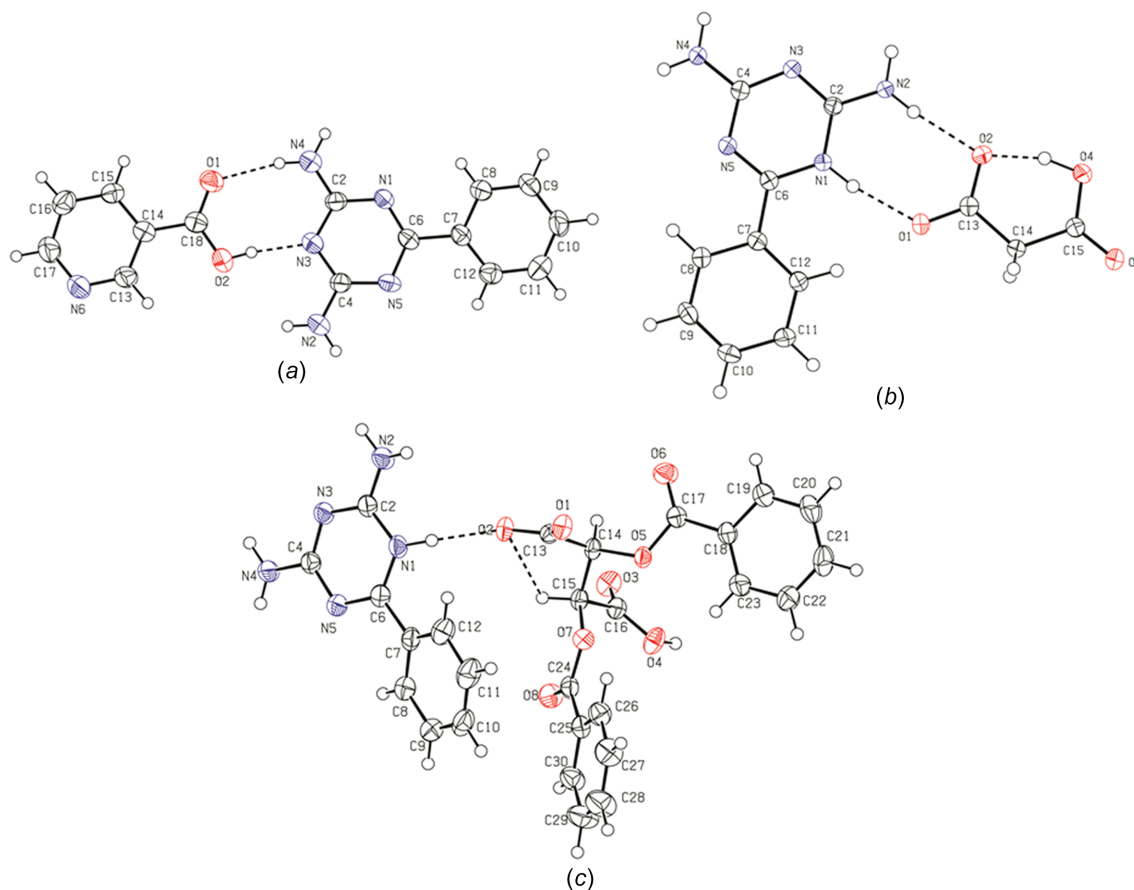


Figure 1

The molecular structures of (a) (I), (b) (II) and (c) (III), with displacement ellipsoids drawn at the 50% probability level.

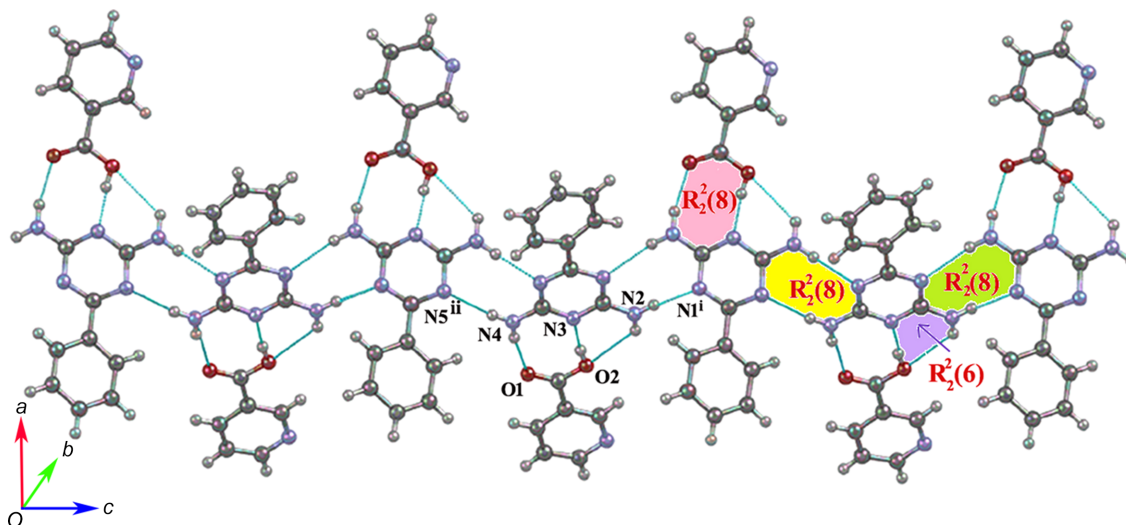


Figure 2

A supramolecular wave-like strand formed by a complementary base pair through $N-H \cdots N$ hydrogen bonds in cocrystal (I) (DAPT-NA). [Symmetry codes: (i) $x - \frac{1}{2}, -y + 2, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$.]

(COOH) and $C(H)(OCOPh)(COO^-)$ groups of DBTA is $62.1(3)^\circ$, suggesting a *gauche* conformation between the groups. This conformation reflects a balance between minimizing steric hindrance and optimizing energetically favourable interactions to achieve optimal overall stability of the ion (Rychlewska & Warzajtis, 2002).

In cocrystal (I), the primary interaction between DAPT and NA occurs through $N-H \cdots O$ and $O-H \cdots N$ hydrogen bonds involving the ring N3 atom of the triazine, the amino N4

atom of DAPT and the carboxyl O1 and O2 atoms of NA. The interactions lead to the generation of a robust $R_2^2(8)$ heterosynthon. The $R_2^2(6)$ ring motif (Bernstein *et al.*, 1995) is formed via $N-H \cdots O$ hydrogen bonds involving ring atom N3 and amino atom N2 of DAPT and carboxyl atom O2 of NA (Table 2). Furthermore, two different complementary base pairings generate $R_2^2(8)$ homosynths on either side through a pair of $N-H \cdots N$ hydrogen bonds. Among the two base pairings, one is formed by linking the amino N2 and ring N1ⁱ

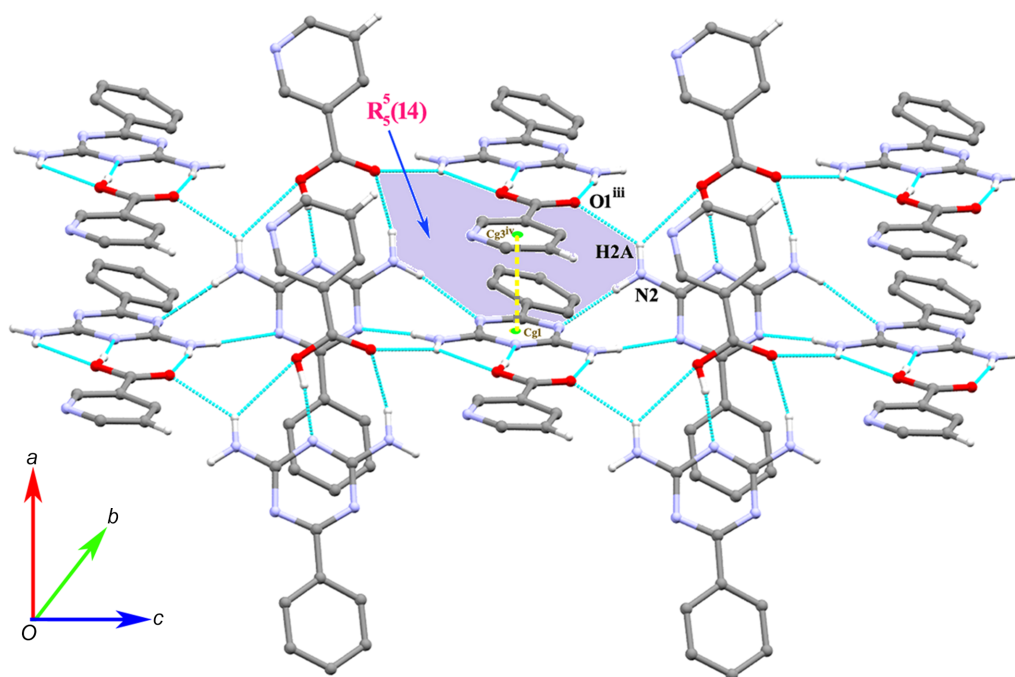
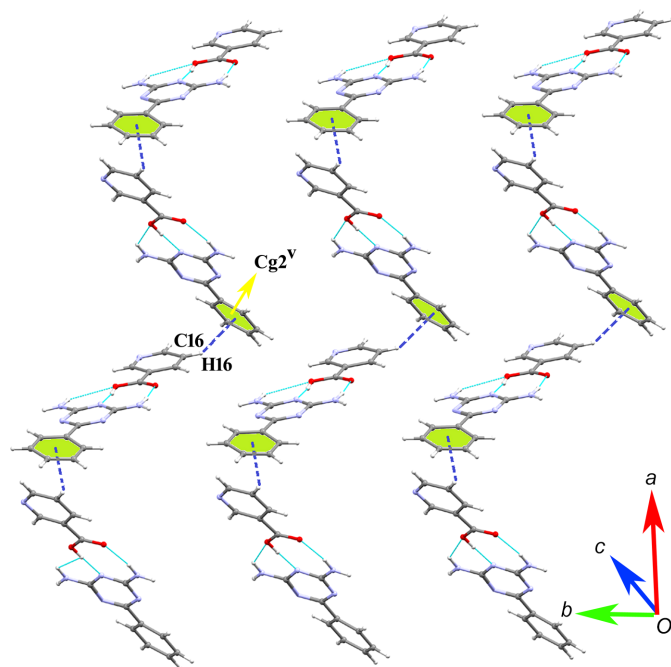


Figure 3

A view of the supramolecular strands in cocrystal (I) (DAPT-NA) interlinked through $N2-H2A \cdots O1^{iii}$ hydrogen bonds [symmetry code: (iii) $x - \frac{1}{2}, -y + 1, z - \frac{1}{2}$] and aromatic $\pi-\pi$ stacking interactions [$Cg1 \cdots Cg3^{iv}$; symmetry code: (iv) $x, y + 1, z$; Cg1 is the centroid of the N1/C2/N3/C4/N5/C6 ring and Cg3 is the centroid of the N6/C13/C14-C17 ring].

**Figure 4**

A view of the zigzag arrangement of C—H... π interactions in cocrystal (I) (DAPT–NA). [Symmetry code: (v) $x - \frac{1}{2}, -y + 1, z + \frac{1}{2}$; Cg2 is the centroid of the C7–C12 ring.]

atoms of complementary DAPT molecules, and the other $R_2^2(8)$ ring motif connects two centrosymmetric DAPT molecules involving the amino N4 and ring N5ⁱⁱ atoms (Etter, 1990; Sundaramoorthy *et al.*, 2014). These centrosymmetric base pairs of DAPT recur and extend as supramolecular wave-like strands (Jyothi *et al.*, 2020) along the *ac* plane (Fig. 2). Two different supramolecular wave-like strands are linked by a pair of N—H...O hydrogen bonds involving the amino N2 atom of DAPT and the carboxyl O1ⁱⁱⁱ atom of NA. The stability of the interlinked strands is further enhanced by the existence of offset aromatic π – π stacking interactions (Cg1...Cg3^{iv}) between the triazine ring of DAPT and the pyridine ring of NA. The corresponding centroid-to-centroid distance, perpendicular distance and slip angle are 3.622 (3) Å, 3.411 (2) Å and 20.3°, respectively, as shown in Fig. 3. This stacking interaction is similar to that reported for nicotinate salts (Balasubramani *et al.*, 2007; Rehman *et al.*, 2018; Sridhar & Ravikumar, 2010). In addition, the crystal packing is stabilized through weak C—H... π interactions (C—H...Cg2^v = 2.95 Å) involving the C16—H16 group of NA and the arene ring of symmetry-related DAPT molecules, as shown in Fig. 4.

Salt (II) is isostructural with a similar reported structure, namely, 2,4-diamino-6-(4-methylphenyl)-1,3,5-triazinium hydrogen malonate (DAMPT–MMA) (Nandy *et al.*, 2016) (see Table S4 of the supporting information). In salt (II), the DAPT and MMA ions interact through a pair of N—H...O hydrogen bonds (Table 3), resulting in a robust $R_2^2(8)$ heteromeric synthon by connecting the protonated ring N1 and amino N2 atoms of the DAPT cation, and the carboxylate O1 and O2 atoms of MMA. Additionally, the MMA anion in the asym-

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...N3	0.85 (6)	1.73 (5)	2.578 (6)	173 (6)
N2—H2A...O1 ⁱⁱⁱ	0.88 (6)	2.27 (7)	2.916 (6)	130 (5)
N2—H2B...N1 ⁱ	0.89 (5)	2.06 (5)	2.940 (6)	178 (8)
N4—H4A...O1	0.91 (6)	1.93 (6)	2.834 (7)	176 (8)
N4—H4B...N5 ⁱⁱ	0.87 (5)	2.42 (7)	3.149 (7)	142 (7)

Symmetry codes: (i) $x - \frac{1}{2}, -y + 2, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + 1, z - \frac{1}{2}$.

Table 3

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1	0.916 (19)	1.877 (19)	2.7831 (16)	169.9 (16)
N2—H2A...O2	0.87 (2)	1.94 (2)	2.8100 (18)	174 (2)
N2—H2B...O4 ⁱ	0.89 (2)	2.21 (2)	2.9690 (17)	144 (2)
N4—H4A...N3 ⁱⁱ	0.89 (2)	2.13 (2)	3.0127 (19)	172 (2)
N4—H4B...O3 ⁱⁱⁱ	0.88 (2)	1.98 (2)	2.8514 (19)	175 (2)
O4—H4C...O2	0.86 (2)	1.63 (2)	2.4598 (16)	161 (2)
C10—H10...O3 ^{iv}	0.95	2.59	3.4305 (19)	147
C12—H12...O1	0.95	2.31	3.2425 (19)	166

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y, -z + 1$; (iii) $x - 1, y - 2, z$; (iv) $-x + 1, y - \frac{3}{2}, -z + \frac{1}{2}$.

metric unit undergoes self-association through intramolecular O—H...O hydrogen bonding, forming an *S*(6) motif (Amirthaganesan *et al.*, 2011). The primary interaction between the ions is also assisted by the presence of a C12—H12...O1 hydrogen bond, which links the DAPT ion and carboxylate O1 atom of the MMA ion. This results in the formation of an $R_1^2(7)$ ring motif, which has a bifurcated O-atom acceptor (Cinčić *et al.*, 2011), through the carbonyl O1 atom of the carboxylate group. The centrosymmetric acid–base aggregate is linked through a pair of N—H...O hydrogen bonds, yielding the $R_6^4(12)$ ring motif by connecting the amino N2 atom of DAPT and carboxyl O4ⁱ atom of the MMA ion. These primary and secondary acid–base interactions, with fused-ring motifs such as $R_2^1(7)$, $R_2^2(8)$, $R_6^4(12)$, $R_2^2(8)$ and $R_1^2(7)$, result in a sextuple *DDDAAD* hydrogen-bonded array (*D* is donor and *A* is acceptor) (Berl *et al.*, 2002) along the *c* axis. The DAPT cations exhibit a discrete complementary base pair through a pair of N—H...N hydrogen bonds by coupling the amino N4 and ring N3ⁱⁱ atoms to generate a robust homomeric $R_2^2(8)$ synthon. The discrete base pair and the sextuple hydrogen-bonded array are held together *via* N—H...N and N—H...O hydrogen bonds by bridging the amino N4 atom of the DAPT cation with a symmetry-related O3ⁱⁱⁱ atom of the MMA anion to render the $R_3^3(10)$ ring motif. This motif exists above and below the discrete base pair, developing a *DADA* quadruple hydrogen-bonded array with a fused-ring sequence of $R_3^3(10)$, $R_2^2(8)$ and $R_3^3(10)$ perpendicular to the sextuple hydrogen-bonded array. The continuous occurrence of these hydrogen-bonded arrays facilitated the formation of continuous tiny rosette-like (Petelski & Fonseca, 2019) supramolecular layers along the *b* axis, as shown in Fig. 5(*a*). The perpendicular supramolecular rosette-like layers are interlinked *via* C—H...O hydrogen bonds by coupling the arene C—H groups of the DAPT cation and the carboxyl O3^{iv} atom of the MMA anion, generating a supramolecular network, as shown

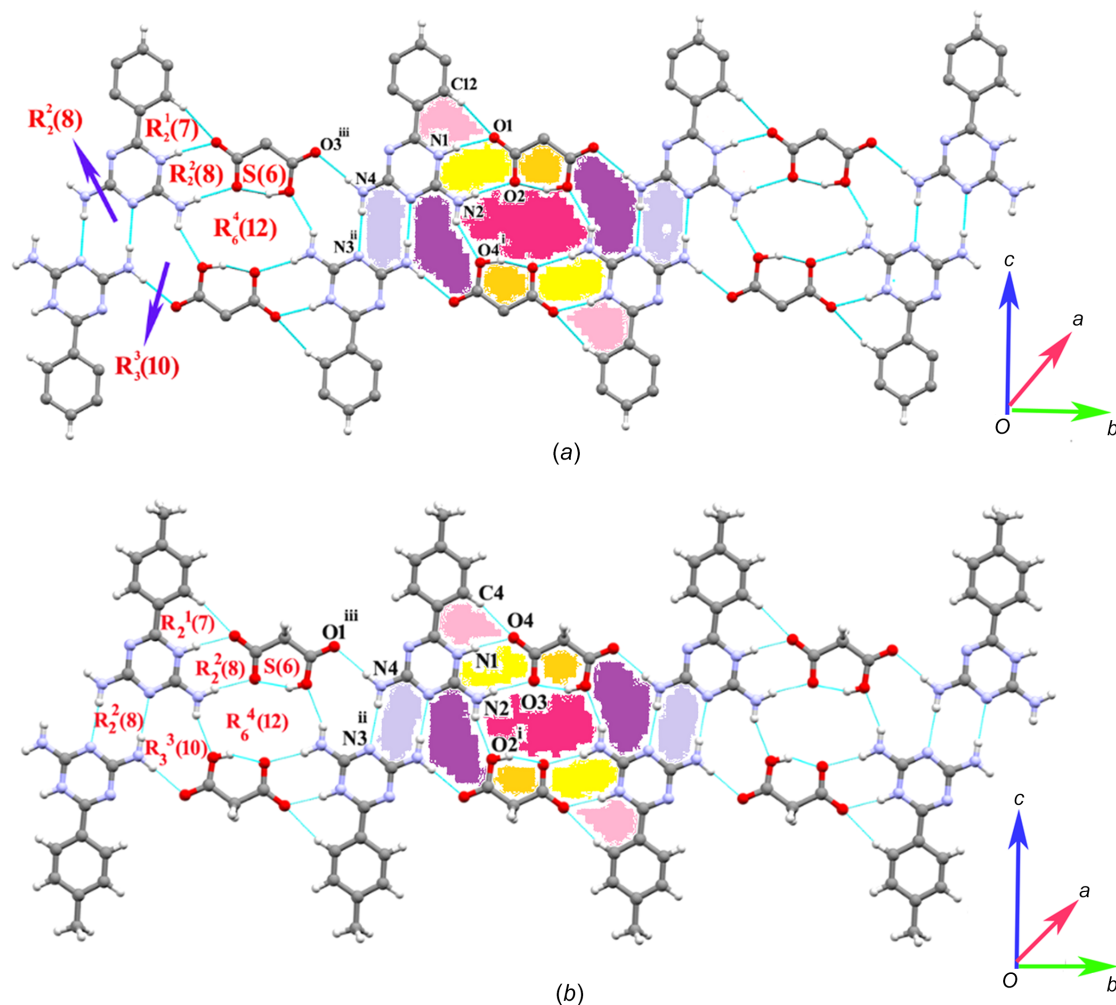


Figure 5

The supramolecular rosette-like architecture formed by sextuple and quadruple hydrogen-bonded arrays in (a) salt (II) (DAPT-MMA) and (b) DAMPT-MMA reported in the literature. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y, -z + 1$; (iii) $x - 1, y - 2, z$.]

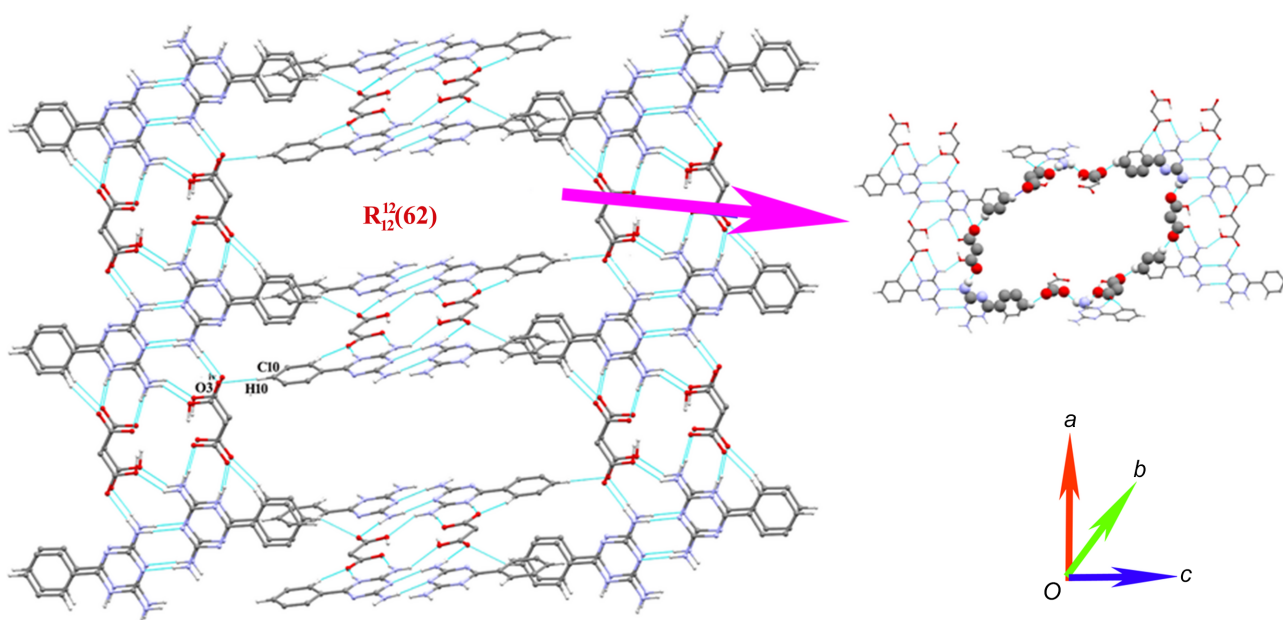


Figure 6

The supramolecular network formed by salt (II) (DAPT-MMA), facilitated through weak C-H...O interactions by interlinking the perpendicular supramolecular layers with a rosette architecture. [Symmetry code: (iv) $-x + 1, y - \frac{3}{2}, -z + \frac{1}{2}$.]

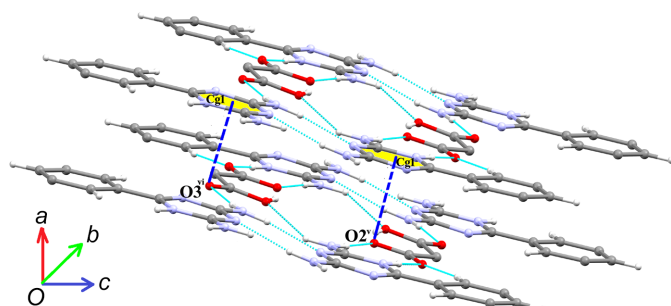


Figure 7

The supramolecular chains forming parallel layers along the *b* axis through carbonyl- π ($\text{C}=\text{O} \cdots \text{Cg1}$) interactions in salt (II) (DAPT-MMA). [Symmetry codes: (v) $x, y + 1, z$; (vi) $x + 1, y + 1, z$; Cg1 is the centroid of the N1/C2/N3/C4/N5/C6 ring.]

in Fig. 6. The stability of parallel layers is enriched by two different weak carbonyl- π interactions between the triazine ring of DAPT (Cg1) and the carboxylate carbonyl ($\text{C13}=\text{O2}^{\text{v}}$) group and the carboxyl carbonyl ($\text{C15}=\text{O3}^{\text{vi}}$) group of the MMA ion. The corresponding carbonyl- π distances are 3.3034 (13) and 3.1426 (12) Å, respectively, as shown in Fig. 7. The hydrogen-bonding patterns and supramolecular architectures are similar to those of the reported DAMPT-MMA [Fig. 5(b)], except for the interlinking of the supramolecular rosette-like layers through $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonding in salt (II), which occurs through van der Waals interactions in the reported DAMPT-MMA.

In salt (III), the DBTA anion undergoes self-association through carboxyl-carboxylate interactions *via* the $\text{O4}-\text{H4C} \cdots \text{O1}^{\text{i}}$ hydrogen bond to generate a supramolecular

Table 4

Hydrogen-bond geometry (Å, °) for (III).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O2}$	0.91 (3)	1.91 (3)	2.745 (3)	152 (3)
$\text{N2}-\text{H2A} \cdots \text{O3}^{\text{iii}}$	0.89 (2)	1.98 (2)	2.856 (3)	169 (2)
$\text{N2}-\text{H2B} \cdots \text{O2}^{\text{vi}}$	0.90 (3)	2.11 (3)	3.008 (3)	178 (2)
$\text{N4}-\text{H4A} \cdots \text{O6}^{\text{vi}}$	0.89 (3)	2.02 (3)	2.901 (3)	170 (3)
$\text{N4}-\text{H4B} \cdots \text{O1}^{\text{ii}}$	0.87 (3)	2.48 (3)	3.037 (3)	123 (2)
$\text{O4}-\text{H4C} \cdots \text{O1}^{\text{i}}$	0.86 (3)	1.62 (3)	2.471 (2)	167 (5)
$\text{C12}-\text{H12} \cdots \text{O8}^{\text{iii}}$	0.95	2.59	3.203 (3)	123
$\text{C14}-\text{H14} \cdots \text{N3}^{\text{viii}}$	1.00	2.35	3.317 (3)	162
$\text{C19}-\text{H19} \cdots \text{O3}^{\text{vii}}$	0.95	2.50	3.363 (3)	152
$\text{C21}-\text{H21} \cdots \text{O8}^{\text{iv}}$	0.95	2.35	3.294 (4)	171

Symmetry codes: (i) $x, y - 1, z$; (ii) $x + 1, y, z$; (iii) $x, y + 1, z$; (iv) $x - 1, y, z$; (v) $-x + 2, y + \frac{1}{2}, -z + 2$; (vi) $-x + 1, y + \frac{1}{2}, -z + 2$; (viii) $-x + 2, y - \frac{1}{2}, -z + 2$.

chain propagating along the *b* axis. Adjacent supramolecular chains are held together by primary acid-base interactions *via* $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 4) by linking of the protonated ring N1 atom of the DAPT ion and the carboxylate O2 atom of the DBTA ion. In addition, adjacent supramolecular chains are connected through a pair of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds by linking the amino N4 and N2 atoms of the DAPT cation with the carboxylate O1ⁱⁱ and carboxyl O3ⁱⁱⁱ atoms of symmetry-related DBTA anions, respectively. Furthermore, the chain is stabilized by acid-acid interactions through weak $\text{C21}-\text{H21} \cdots \text{O8}^{\text{iv}}$ interactions by coupling of a symmetry-related arene $\text{C}-\text{H}$ group and the benzoyl group of the DBTA anion.

The primary and secondary acid-base interactions lead to the formation of fused $R_3^3(12)$, $R_4^3(26)$ and $R_3^3(24)$ ring motifs, and thus generate supramolecular layers extending along the *ac* plane, as shown in Fig. 8. The stability of the supra-

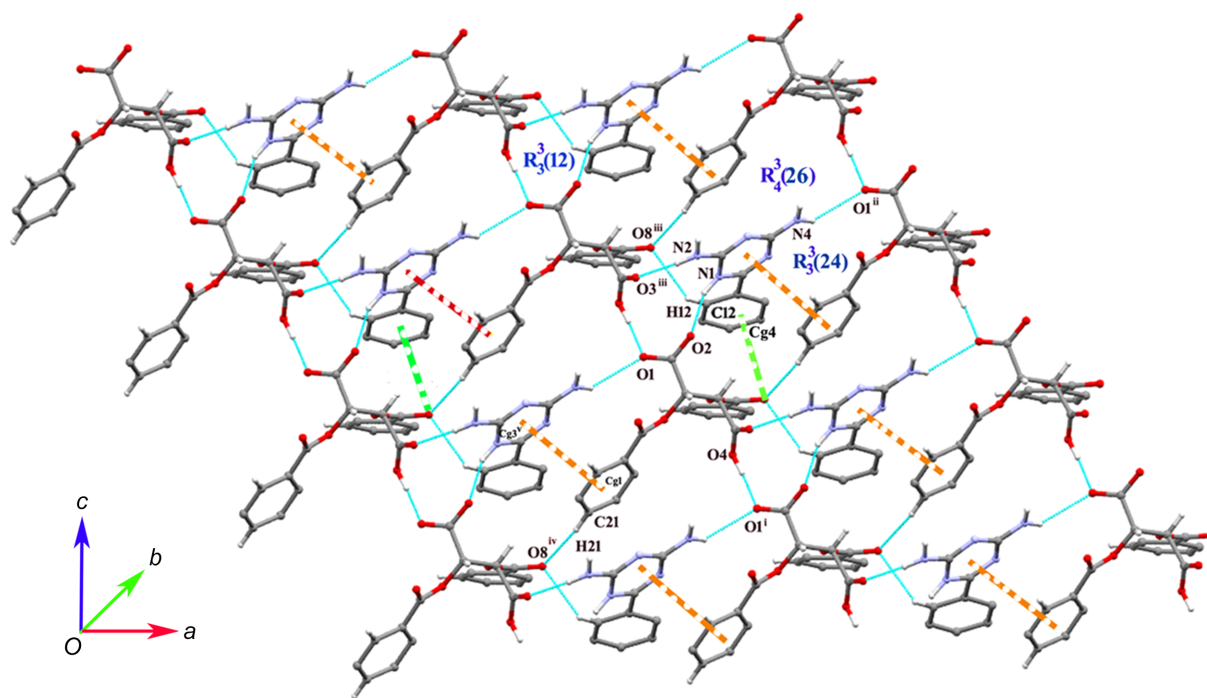


Figure 8

The supramolecular layer extending along the *ac* plane *via* carboxyl-carboxylate, acid-base, stacking ($\text{Cg1} \cdots \text{Cg3}^{\text{v}}$) and carbonyl- π ($\text{C}=\text{O} \cdots \text{Cg4}$) interactions in salt (III) (DAPT-DBTA). [Symmetry codes: (i) $x, y - 1, z$; (ii) $x + 1, y, z$; (iii) $x, y + 1, z$; (iv) $x - 1, y, z$; (v) $x - 1, y - 1, z$; Cg1 is the centroid of the C18-C23, Cg3 of the N1/O2/N3/O4/N5/O6 ring and Cg4 of the C7-C12 ring.]

molecular layers is enhanced by offset aromatic π – π stacking interactions and carbonyl– π interactions. Aromatic π – π stacking interactions (Rychlewska & Warżajtis, 2001) are observed between the arene ring of the DBTA anion and the triazine ring of the DAPT cation ($Cg1 \cdots Cg3^v$), with a centroid-to-centroid distance of 3.8130 (16) Å, a perpendicular distance of 3.4584 (12) Å and a slip angle of 30.3°. The carbonyl– π interaction ($C24=O8 \cdots Cg4$) is observed in the asymmetric unit itself, which occurs between the carbonyl group of the benzoyl group of the DBTA ion and the arene ring of the DAPT ion at a distance of 3.970 (2) Å. In addition, there is a $C-H \cdots \pi$ interaction between an arene $C-H$ group of DAPT and the aromatic π -cloud of the DBTA anion in the asymmetric unit, and, furthermore, the DBTA ion forms a weak intramolecular $C-H \cdots O$ hydrogen bond, thus generating an $S(5)$ ring motif (Motherwell *et al.*, 1999), as shown in Fig. 1(c).

The supramolecular layers are interlinked by a supramolecular tunnel extending along the b axis. This tunnel is made up of a pair of strong $N-H \cdots O$ hydrogen bonds by coupling the amino N2 and N4 atoms of one DAPT ion with the carboxylate $O2^{vi}$ and benzoyl $O6^{vi}$ atoms of one DBTA anion, respectively. Furthermore, the layers are linked together by weak $C19-H19 \cdots O3^{vii}$ and $C14-H14 \cdots N3^{viii}$ hydrogen bonds. These hydrogen bonds connect the arene $C-H$ and methylene $C-H$ groups of the DBTA anion with the carboxyl $O3$ atom of the DBTA anion and the ring N3 atom of the symmetry-related DAPT cation, respectively. These interactions facilitate the generation of the fused-ring motifs $R_2^2(8)$, $R_2^2(9)$, $R_4^3(13)$, $R_3^3(17)$ and $R_3^3(21)$, as shown in Fig. 9. These fused-ring motifs can be the building blocks of a supramolecular tunnel-like architecture (Manin *et al.*, 2018). Furthermore, the tunnel is strengthened by the presence of a $C-H \cdots \pi$ interaction [$C27-H27 \cdots Cg2^{ix}$; symmetry code:

$-x + 1, y + \frac{1}{2}, -z + 1$], which occurs between two symmetry-related DBTA anions.

The crystal structures of (I)–(III) reveal distinct supramolecular architectures influenced by protonation and intramolecular and intermolecular interactions which govern the crystal packing. In all three compounds, the various donor and acceptor groups facilitate the generation of diverse supramolecular architectures, including supramolecular strands in (I), supramolecular rosettes in (II) and a supramolecular tunnel-like structure in (III).

3.2. Hirshfeld surface analysis

Hirshfeld surfaces (HSs) (McKinnon *et al.*, 2007; Spackman & Jayatilaka, 2009) can be visualized and analysed to study the intermolecular interactions in the crystal. For (I)–(III), the Hirshfeld isosurface is defined by the isovalue of $w(r) = 0.5$, mapped over d_{norm} , which is the sum of the normalized extensions from a chosen point on the HS to the interior (d_i) and exterior (d_e) atoms between the arbitrary units (−0.54 to 1.17), (−0.59 to 1.03) and (−0.86 to 1.38), respectively. For the HSs of all the compounds, the red colour indicates the strongest hydrogen-bonded interactions, the blue colour signifies interactions equal to the sum of the van der Waals radii of the atoms in close contact and the white colour represents interactions less than the sum of the van der Waals radii of the atoms in close proximity.

The promolecules of (I)–(III) surrounded by exterior molecules in the HS are shown in Figs. 10(a)–(c). The intensity of the red patches is proportional to the strength of the interaction energy, which varies with the hydrogen-bond distance and angle of the hydrogen-bond framework. The atoms within 3.8 Å of the HS with all possible strong intermolecular hydrogen-bond interactions of types $N-H \cdots O$,

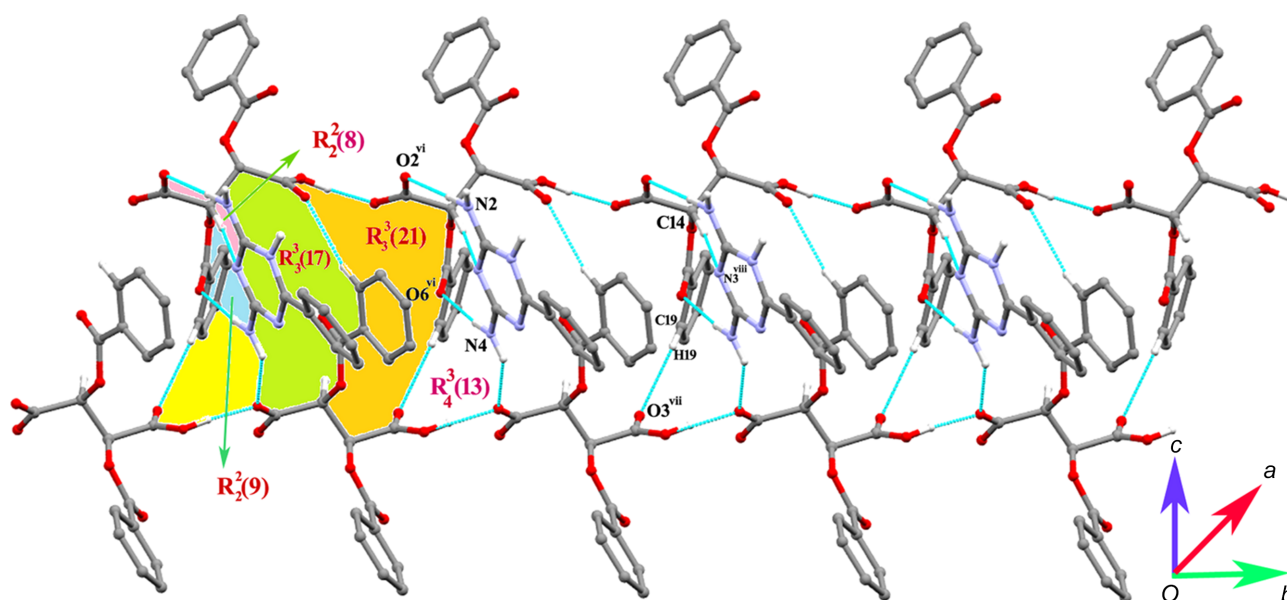


Figure 9

The supramolecular tunnel extending along the b axis through $N-H \cdots O$, $C-H \cdots O$ and $C-H \cdots N$ hydrogen bonds in salt (III) (DAPT–DBTA). [Symmetry codes: (vi) $-x + 2, y + \frac{1}{2}, -z + 2$; (vii) $-x + 1, y + \frac{1}{2}, -z + 2$; (viii) $-x + 2, y - \frac{1}{2}, -z + 2$.]

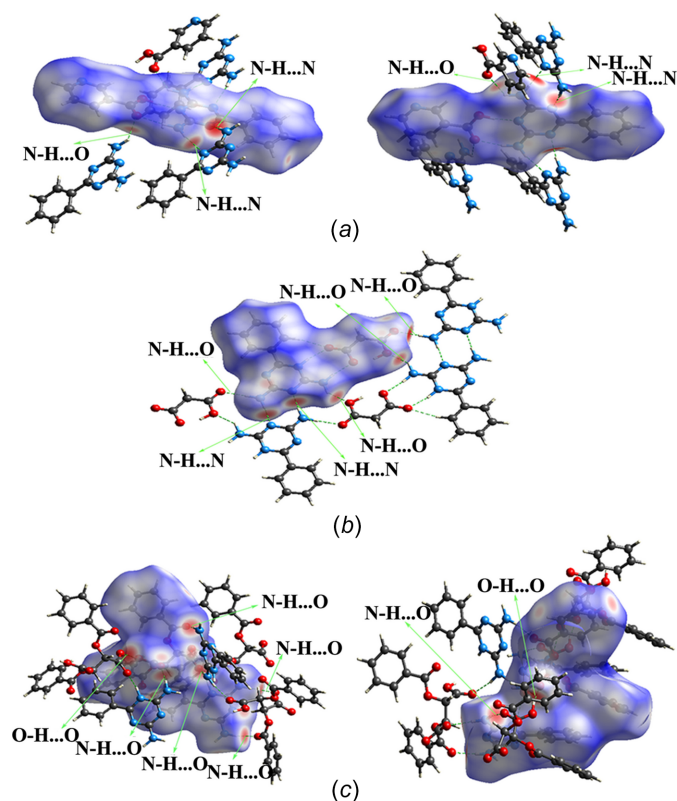


Figure 10
Hirshfeld surfaces for (a) (I), (b) (II) and (c) (III) mapped with d_{norm} .

$\text{N}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{O}$ are displayed in the HS mapped over d_{norm} .

In cocrystal (I) and salt (II), the promolecule within the HS has potential sites for intermolecular hydrogen-bonding

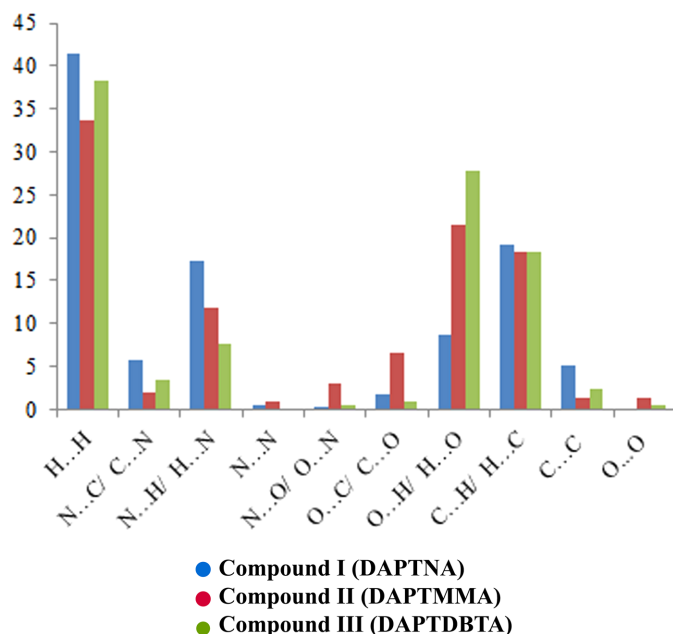


Figure 11
Comparison of the percentage distributions of various intermolecular interactions in (I)–(III).

interactions with the nearby surrounding DAPT and NA/MMA molecules at the exterior of the HS through $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ interactions. These interactions, in the case of cocrystal (I), connect the amino N2 hydrogen-bond donor of DAPT with the carboxylate O1 atom of NA and the ring N1 atom of DAPT, and the amino N4 atom with the ring N5 atom of the DAPT hydrogen-bond donor and acceptors, respectively. In salt (II), the amino N2 hydrogen-bond donor of DAPT is linked with the carboxyl O4 atom of MMA, and the amino N4 connects the ring N3 atom of DAPT and the carboxyl O3 atom of the MMA hydrogen-bond donor and acceptor, respectively. Whereas in salt (III), the promolecule interacts with exterior molecules through strong $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding, which connects the amino N2 and N4 hydrogen-bond donors of DAPT and the carboxyl O4 hydrogen-bond donor with the O3/O2, O6 and O1 hydrogen-bond acceptor atoms of DBTA, respectively.

The total intermolecular interactions between the promolecule and the exterior molecules in the HS for (I)–(III) are quantified via 2D fingerprint plots in terms of d_i and d_e , and are represented in blue-coloured regions with dots of various intensities (see Figs. S1, S2 and S3 of the supporting information).

The fingerprint plots of all three compounds revealed that among all the noncovalent interactions, $\text{H}\cdots\text{H}$ contacts contributed the maximum to the crystal packing of the structures, as shown in Fig. 11. Cocrystal (I) exhibits the maximum contribution of $\text{H}\cdots\text{H}$ contacts (41.5%), indicating close packing. Salts (II) and (III) exhibit the highest contributions of $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts (21.6 and 27.8%, respectively) and facilitated hydrogen bonding involving O atoms. The $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ contacts are quite important, especially in cocrystal (I), with a 17.4% contribution to the strong hydrogen bonding involving N and H atoms. The $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ and $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ interactions play a vital role in building strong hydrogen-bonding contributions to the crystal stability of all three compounds. The $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ contacts [19.1, 18.3 and 18.4% for (I)–(III), respectively] play a crucial role across all three compounds, indicating the common interactions between C and H atoms. Thus, the fingerprint plots reveal the complex and varied nature of the intermolecular interactions that define the stability and packing of these crystal structures.

The shape index is a qualitative measurement of the shape of a promolecule. The convexity of the blue-coloured shape shows the hydrogen-bond interaction of the donor-type regions, whereas the red concave region acts as an acceptor. The aromatic stacking in the crystal packing appears as closely arranged red and blue triangles facing each other on the HS (see Fig. S4 of the supporting information). The curvedness is a function of the r.m.s. curvature of the surface. The flat region has low coordination, whereas the curved region has higher coordination.

3.3. Comparative study of the reported crystal structures

A total of 31 reported crystal structures have been taken for comparison with the present work (see Table S5 of the

supporting information). The labels a–ae provide details of the reported structures, which are solvates, salts and cocrystals of various carboxylic acids with N-heterocyclic ligands as follows: (a–e) solvates and salts of DAPT, (f–n) salts and cocrystals of nicotinic acid, (o–u) salts and cocrystals of malonic acid, and (v–ae) cocrystals, salts and derivatives of DBTA. The unit-cell parameters, protonation site, noncovalent interactions, predominant hydrogen-bonded motifs and resulting supramolecular architectures are compared with the current work.

The existence of reported salts and cocrystals are predicted from the $\Delta D(C-O)$ parameters and it was found that 11 of the reported structures (labelled e, h, i, j, k, l, m, n, o, r and t) are in the range of salts (<0.03 Å) and eight structures (labelled a, d, g, p, s, u, v and w) are in the range of cocrystals (>0.08 Å), and they revealed consistency with the reported literature (Mekala *et al.*, 2018).

The primary acid–base hydrogen-bonded interactions resulted in the formation of an $R_2^2(8)$ primary ring motif *via* a pair of $N-H\cdots O$ and $N-H\cdots N$ hydrogen bonds, and a mixture of ($N-H\cdots O$ and $N-H\cdots N$)/($N-H\cdots O$ and $C-H\cdots O$), and was observed in 14 reported structures (labelled a, c, d, e, h–m and o–r); this is similar to the motifs observed in (I) and (II). Complementary base pairing was evident in 12 structures, among which nine structures (labelled a–c, g, i, j, o, q and r) exhibit homodimeric $R_2^2(8)$ motifs *via* $N-H\cdots N$ hydrogen bonds, two (labelled e and p) generate $R_2^2(8)$ and $R_2^2(12)$ motifs, respectively, through $N-H\cdots O$ interactions, and one (labelled u) forms an $R_2^2(10)$ motif *via* $C-H\cdots N$ hydrogen bonds. Furthermore, the $R_3^3(10)$ ring motif was identified in five crystal structures (labelled c, e, o, p and r), consistent with salt (II). The intramolecular hydrogen-bonded ring motif $S(6)$ was identified in five malonic acid/malonate structures (labelled e, p, q, r and t), resembling salt (II), while seven DBTA cocrystals and solvates (labelled x–aa and ac–ae) exhibit an $S(5)$ motif, similar to salt (III). Bifurcated hydrogen bonds lead to $R_2^1(7)$ motifs, which are observed in three malonic acid–base systems (labelled e, s and t), analogous to salt (II). Furthermore, offset aromatic π – π stacking interactions are observed in seven of the reported derivatives of NA (labelled f, g, i, k, l, m and n), as exhibited by cocrystal (I), and three of the reported DBTA structures (labelled z, aa and ab) resemble salt (III). $C-H\cdots\pi$ interactions are exhibited by two of the reported structures (labelled i and j), as in cocrystal (I), and three DBTA derivatives (labelled v, w and ac), as shown by salt (III). Carbonyl– π stacking is involved in five crystal structures of malonic acid (labelled o, p, r, s and u), similar to salt (II). The cumulative contribution of the interactions lead to various supramolecular architectures, such as the rosette-like arrangement in DAMPT–MMA (labelled e), that closely resemble salt (II).

4. Conclusion

The presence of different functional groups in the counterions (NA, MMA and DBTA) influences the types and strengths of the supramolecular interactions and thus results

in distinct supramolecular synthons and unique supramolecular architectures. A detailed investigation of the resulting supramolecular interactions of (I)–(III) and those in the literature provide insights into the design and development of their derivatives with potential applications in pharmaceuticals. Hirshfeld surface analysis quantifies the major type of supramolecular interaction that enables close packing of the molecule in the crystal.

5. Related literature

The following references are cited in the supporting information: Chappa *et al.* (2019); Chen *et al.* (2003); Delori *et al.* (2008); Froschauer & Weil (2012); Kastelic *et al.* (2013); Lee & Wang (2010); O'Malley *et al.* (2021); Sangavi *et al.* (2024); Sendh *et al.* (2021); Sridhar & Ravikumar (2011); Thanigaimani *et al.* (2007, 2013); Wang *et al.* (2005, 2015); Zhang *et al.* (2007).

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Structural and supramolecular insights into crystalline multicomponent systems of 2,4-diamino-6-phenyl-1,3,5-triazine with various carboxylic acids

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Computing details

6-Phenyl-1,3,5-triazine-2,4-diamine–pyridine-3-carboxylic acid (1/1) (I)

Crystal data

$C_9H_9N_5 \cdot C_6H_5NO_2$

$M_r = 310.32$

Monoclinic, Pn

Hall symbol: $P -2yac$

$a = 9.2901$ (9) Å

$b = 7.2116$ (8) Å

$c = 11.5857$ (12) Å

$\beta = 111.016$ (4)°

$V = 724.57$ (13) Å³

$Z = 2$

$F(000) = 324$

$D_x = 1.422$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2549 reflections

$\theta = 2.4$ – 25.0°

$\mu = 0.10$ mm⁻¹

$T = 173$ K

Block, colourless

$0.14 \times 0.11 \times 0.06$ mm

Data collection

Bruker APEX IV CCD

diffractometer

Radiation source: microfocus sealed X-ray tube

Mirror optics monochromator

φ and ω scans

11335 measured reflections

2549 independent reflections

2244 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$

$h = -11 \rightarrow 11$

$k = -8 \rightarrow 8$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.174$

$S = 1.09$

2549 reflections

228 parameters

9 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$W = 1/[\Sigma^2(FO^2) + (0.1051P)^2 + 0.1414P]$

WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.49$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Absolute structure: Flack (1983)

Absolute structure parameter: 0.500

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating -R-factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.6639 (5)	1.0112 (6)	0.5551 (4)	0.0333 (12)
N2	0.2884 (5)	0.8059 (7)	0.2977 (4)	0.0444 (14)
N3	0.4743 (5)	0.7776 (6)	0.4912 (4)	0.0392 (14)
N4	0.6697 (6)	0.7576 (7)	0.6794 (4)	0.0462 (16)
N5	0.4670 (5)	1.0426 (6)	0.3592 (4)	0.0360 (11)
O1	0.5142 (4)	0.4203 (6)	0.6816 (4)	0.0467 (12)
O2	0.3339 (5)	0.4709 (6)	0.4958 (4)	0.0503 (12)
C2	0.6026 (6)	0.8501 (7)	0.5747 (4)	0.0356 (16)
C4	0.4120 (6)	0.8759 (7)	0.3843 (4)	0.0340 (16)
C6	0.5949 (5)	1.1000 (7)	0.4493 (4)	0.0318 (14)
C7	0.6660 (5)	1.2756 (7)	0.4313 (4)	0.0329 (16)
C8	0.8187 (7)	1.3133 (9)	0.5073 (5)	0.0480 (19)
C9	0.8899 (8)	1.4734 (10)	0.4930 (5)	0.0586 (19)
C10	0.8107 (7)	1.6006 (9)	0.4042 (6)	0.054 (2)
C11	0.6619 (7)	1.5649 (9)	0.3270 (6)	0.0488 (19)
C12	0.5908 (6)	1.4011 (8)	0.3405 (5)	0.0405 (17)
N6	0.1099 (7)	−0.0156 (9)	0.5052 (5)	0.065 (2)
C13	0.1856 (7)	0.1437 (9)	0.5044 (5)	0.0468 (19)
C14	0.3195 (5)	0.1954 (7)	0.5979 (4)	0.0330 (14)
C15	0.3803 (6)	0.0772 (8)	0.6990 (5)	0.0379 (16)
C16	0.3024 (7)	−0.0856 (9)	0.7020 (5)	0.050 (2)
C17	0.1681 (8)	−0.1241 (11)	0.6040 (6)	0.063 (2)
C18	0.3975 (6)	0.3736 (8)	0.5948 (5)	0.0361 (17)
H2A	0.237 (7)	0.710 (7)	0.309 (6)	0.06 (2)*
H2B	0.253 (7)	0.862 (9)	0.225 (4)	0.06 (2)*
H4A	0.618 (7)	0.650 (7)	0.676 (7)	0.08 (2)*
H4B	0.757 (5)	0.756 (12)	0.741 (5)	0.09 (3)*
H8	0.87335	1.22688	0.56949	0.0580*
H9	0.99387	1.49673	0.54432	0.0700*
H10	0.85916	1.71340	0.39632	0.0640*
H11	0.60800	1.65168	0.26479	0.0590*
H12	0.48872	1.37547	0.28609	0.0480*
H2	0.384 (8)	0.568 (6)	0.491 (7)	0.07 (2)*
H13	0.14426	0.22454	0.43566	0.0560*
H15	0.47343	0.10758	0.76466	0.0460*

H16	0.34050	−0.16866	0.76984	0.0600*
H17	0.11408	−0.23454	0.60732	0.0750*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.030 (2)	0.033 (2)	0.034 (2)	−0.0041 (16)	0.0078 (17)	−0.0026 (17)
N2	0.038 (2)	0.047 (3)	0.042 (2)	−0.011 (2)	0.007 (2)	−0.005 (2)
N3	0.036 (2)	0.041 (3)	0.038 (2)	−0.0062 (19)	0.0100 (19)	−0.0037 (19)
N4	0.043 (3)	0.044 (3)	0.043 (2)	−0.005 (2)	0.005 (2)	0.001 (2)
N5	0.030 (2)	0.045 (2)	0.0280 (19)	−0.0035 (19)	0.0044 (17)	−0.0047 (19)
O1	0.034 (2)	0.044 (2)	0.053 (2)	0.0001 (15)	0.0046 (18)	0.0003 (18)
O2	0.044 (2)	0.041 (2)	0.059 (2)	−0.0106 (18)	0.010 (2)	0.004 (2)
C2	0.032 (3)	0.037 (3)	0.033 (2)	0.002 (2)	0.006 (2)	0.001 (2)
C4	0.032 (3)	0.034 (3)	0.033 (2)	0.001 (2)	0.008 (2)	−0.001 (2)
C6	0.027 (2)	0.038 (3)	0.033 (2)	−0.0031 (19)	0.014 (2)	−0.007 (2)
C7	0.033 (3)	0.038 (3)	0.031 (2)	−0.006 (2)	0.0156 (19)	−0.004 (2)
C8	0.043 (3)	0.057 (4)	0.037 (3)	−0.015 (3)	0.006 (2)	0.008 (2)
C9	0.047 (3)	0.067 (4)	0.050 (3)	−0.027 (3)	0.003 (3)	0.007 (3)
C10	0.060 (4)	0.053 (4)	0.049 (3)	−0.023 (3)	0.020 (3)	0.004 (3)
C11	0.055 (4)	0.047 (3)	0.046 (3)	0.006 (3)	0.020 (3)	0.010 (3)
C12	0.035 (3)	0.048 (3)	0.039 (3)	−0.002 (2)	0.014 (2)	−0.001 (2)
N6	0.065 (4)	0.075 (4)	0.042 (3)	−0.033 (3)	0.005 (2)	0.007 (3)
C13	0.046 (3)	0.058 (4)	0.033 (3)	−0.012 (3)	0.010 (2)	0.002 (2)
C14	0.030 (2)	0.040 (3)	0.032 (2)	0.000 (2)	0.0149 (19)	−0.006 (2)
C15	0.035 (3)	0.045 (3)	0.032 (2)	0.004 (2)	0.010 (2)	0.002 (2)
C16	0.054 (4)	0.054 (4)	0.043 (3)	−0.001 (3)	0.019 (3)	0.011 (3)
C17	0.067 (4)	0.067 (4)	0.050 (4)	−0.027 (3)	0.015 (3)	0.006 (3)
C18	0.032 (3)	0.039 (3)	0.037 (3)	0.004 (2)	0.012 (2)	−0.003 (2)

Geometric parameters (Å, °)

N1—C2	1.349 (7)	C10—C11	1.375 (10)
N1—C6	1.327 (6)	C11—C12	1.389 (9)
N2—C4	1.324 (7)	O2—H2	0.85 (6)
N3—C2	1.343 (7)	N6—C17	1.331 (9)
N3—C4	1.363 (6)	N6—C13	1.349 (9)
N4—C2	1.328 (6)	C8—H8	0.9500
N5—C4	1.378 (7)	C9—H9	0.9500
N5—C6	1.335 (7)	C10—H10	0.9500
O1—C18	1.232 (7)	C11—H11	0.9500
N2—H2A	0.88 (6)	C12—H12	0.9500
O2—C18	1.293 (7)	C13—C14	1.376 (8)
N2—H2B	0.89 (5)	C14—C15	1.394 (7)
N4—H4B	0.87 (5)	C14—C18	1.482 (8)
N4—H4A	0.91 (6)	C15—C16	1.386 (9)
C6—C7	1.477 (7)	C16—C17	1.381 (9)
C7—C12	1.374 (7)	C13—H13	0.9500

C7—C8	1.402 (8)	C15—H15	0.9500
C8—C9	1.370 (10)	C16—H16	0.9500
C9—C10	1.378 (9)	C17—H17	0.9500
C2—N1—C6	118.6 (4)	C9—C8—H8	120.00
C2—N3—C4	115.5 (4)	C7—C8—H8	120.00
C4—N5—C6	113.5 (4)	C8—C9—H9	120.00
N1—C2—N3	122.2 (4)	C10—C9—H9	120.00
N1—C2—N4	119.9 (5)	C11—C10—H10	120.00
N3—C2—N4	117.9 (5)	C9—C10—H10	120.00
C4—N2—H2B	118 (4)	C10—C11—H11	120.00
H2A—N2—H2B	118 (6)	C12—C11—H11	120.00
C4—N2—H2A	124 (4)	C11—C12—H12	120.00
N3—C4—N5	125.2 (5)	C7—C12—H12	120.00
C2—N4—H4B	139 (5)	N6—C13—C14	123.5 (5)
N2—C4—N3	117.4 (5)	C13—C14—C15	118.4 (5)
N2—C4—N5	117.3 (4)	C13—C14—C18	121.9 (5)
H4A—N4—H4B	110 (7)	C15—C14—C18	119.8 (5)
C2—N4—H4A	109 (5)	C14—C15—C16	118.8 (5)
N5—C6—C7	118.2 (4)	C15—C16—C17	118.4 (6)
N1—C6—C7	116.9 (4)	N6—C17—C16	123.9 (7)
N1—C6—N5	124.9 (5)	O1—C18—C14	120.8 (5)
C6—C7—C8	118.7 (4)	O2—C18—C14	114.9 (5)
C6—C7—C12	122.9 (5)	O1—C18—O2	124.4 (5)
C8—C7—C12	118.4 (5)	N6—C13—H13	118.00
C7—C8—C9	120.7 (5)	C14—C13—H13	118.00
C8—C9—C10	120.0 (6)	C14—C15—H15	121.00
C9—C10—C11	120.3 (6)	C16—C15—H15	121.00
C10—C11—C12	119.6 (6)	C15—C16—H16	121.00
C7—C12—C11	121.0 (5)	C17—C16—H16	121.00
C18—O2—H2	115 (5)	N6—C17—H17	118.00
C13—N6—C17	117.1 (6)	C16—C17—H17	118.00
C6—N1—C2—N3	−0.3 (8)	C6—C7—C12—C11	179.9 (5)
C6—N1—C2—N4	179.6 (5)	C8—C7—C12—C11	−2.4 (8)
C2—N1—C6—N5	0.4 (8)	C7—C8—C9—C10	0.8 (10)
C2—N1—C6—C7	−179.8 (5)	C8—C9—C10—C11	−2.1 (10)
C4—N3—C2—N1	1.3 (8)	C9—C10—C11—C12	1.1 (10)
C4—N3—C2—N4	−178.6 (5)	C10—C11—C12—C7	1.2 (9)
C2—N3—C4—N2	177.7 (5)	C17—N6—C13—C14	1.6 (10)
C2—N3—C4—N5	−2.5 (8)	C13—N6—C17—C16	−2.2 (11)
C6—N5—C4—N2	−177.7 (5)	N6—C13—C14—C15	−0.1 (9)
C6—N5—C4—N3	2.5 (8)	N6—C13—C14—C18	−178.7 (6)
C4—N5—C6—N1	−1.4 (7)	C13—C14—C15—C16	−0.9 (8)
C4—N5—C6—C7	178.8 (4)	C18—C14—C15—C16	177.7 (5)
N1—C6—C7—C8	16.9 (7)	C13—C14—C18—O1	177.3 (6)
N1—C6—C7—C12	−165.4 (5)	C13—C14—C18—O2	−2.9 (8)
N5—C6—C7—C8	−163.3 (5)	C15—C14—C18—O1	−1.3 (8)

N5—C6—C7—C12	14.5 (7)	C15—C14—C18—O2	178.5 (5)
C6—C7—C8—C9	179.3 (5)	C14—C15—C16—C17	0.4 (9)
C12—C7—C8—C9	1.4 (8)	C15—C16—C17—N6	1.3 (11)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O2—H2 $\cdots$ N3	0.85 (6)	1.73 (5)	2.578 (6)	173 (6)
N2—H2 <i>A</i> $\cdots$ O1 ⁱ	0.88 (6)	2.27 (7)	2.916 (6)	130 (5)
N2—H2 <i>B</i> $\cdots$ N1 ⁱⁱ	0.89 (5)	2.06 (5)	2.940 (6)	178 (8)
N4—H4 <i>A</i> $\cdots$ O1	0.91 (6)	1.93 (6)	2.834 (7)	176 (8)
N4—H4 <i>B</i> $\cdots$ N5 ⁱⁱⁱ	0.87 (5)	2.42 (7)	3.149 (7)	142 (7)
C8—H8 $\cdots$ N1	0.95	2.45	2.774 (8)	100
C13—H13 $\cdots$ O2	0.95	2.42	2.752 (8)	100

Symmetry codes: (i) $x-1/2, -y+1, z-1/2$; (ii) $x-1/2, -y+2, z-1/2$; (iii) $x+1/2, -y+2, z+1/2$.

2,4-Diamino-6-phenyl-1,3,5-triazin-1-ium hydrogen malonate (II)*Crystal data*

$C_9H_{10}N_5^+ \cdot C_3H_3O_4^-$

$M_r = 291.27$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 8.3350$ (8) Å

$b = 5.1168$ (4) Å

$c = 29.100$ (2) Å

$\beta = 93.188$ (3)°

$V = 1239.15$ (18) Å³

$Z = 4$

$F(000) = 608$

$D_x = 1.561$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2183 reflections

$\theta = 2.4$ – 25.4°

$\mu = 0.12$ mm⁻¹

$T = 173$ K

Block, colourless

$0.16 \times 0.11 \times 0.06$ mm

Data collection

Bruker APEX IV CCD

diffractometer

Radiation source: microfocus sealed X-ray tube

Mirror optics monochromator

φ and ω scans

24363 measured reflections

2183 independent reflections

1895 reflections with $I > 2\sigma(I)$

$R_{int} = 0.077$

$\theta_{max} = 25.0^\circ$, $\theta_{min} = 2.5^\circ$

$h = -9 \rightarrow 9$

$k = -6 \rightarrow 6$

$l = -34 \rightarrow 34$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.103$

$S = 1.06$

2183 reflections

214 parameters

7 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$W = 1/[\Sigma^2(FO^2) + (0.0416P)^2 + 0.4364P]$

WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.22$ e Å⁻³

$\Delta\rho_{min} = -0.28$ e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors.

Weighted R-factors wR and all goodnesses of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating $-R$ -factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.27796 (15)	0.2870 (2)	0.39445 (4)	0.0199 (4)
N2	0.32986 (16)	0.4720 (3)	0.46594 (4)	0.0238 (4)
N3	0.15120 (15)	0.1317 (2)	0.45936 (4)	0.0214 (4)
N4	−0.01786 (16)	−0.2174 (3)	0.44770 (5)	0.0244 (4)
N5	0.11280 (15)	−0.0784 (2)	0.38555 (4)	0.0210 (4)
O1	0.49992 (13)	0.6613 (2)	0.36995 (4)	0.0272 (3)
C2	0.25216 (17)	0.2957 (3)	0.44054 (5)	0.0197 (4)
O2	0.54023 (14)	0.8611 (2)	0.43729 (4)	0.0305 (4)
O3	0.85002 (13)	1.3874 (2)	0.38776 (4)	0.0273 (3)
C4	0.08454 (17)	−0.0509 (3)	0.43110 (5)	0.0200 (4)
O4	0.70822 (15)	1.2555 (2)	0.44525 (4)	0.0282 (4)
C6	0.20494 (17)	0.0962 (3)	0.36801 (5)	0.0192 (4)
C7	0.22972 (17)	0.0868 (3)	0.31809 (5)	0.0204 (4)
C8	0.15057 (19)	−0.1097 (3)	0.29231 (5)	0.0254 (5)
C9	0.1664 (2)	−0.1237 (3)	0.24532 (5)	0.0286 (5)
C10	0.2618 (2)	0.0534 (3)	0.22367 (5)	0.0268 (5)
C11	0.3416 (2)	0.2463 (3)	0.24906 (5)	0.0280 (5)
C12	0.32493 (19)	0.2650 (3)	0.29606 (5)	0.0248 (5)
C13	0.56504 (18)	0.8314 (3)	0.39491 (5)	0.0214 (4)
C14	0.68191 (18)	1.0175 (3)	0.37349 (5)	0.0226 (4)
C15	0.75355 (18)	1.2365 (3)	0.40288 (5)	0.0209 (4)
H1	0.346 (2)	0.408 (4)	0.3829 (6)	0.029 (5)*
H2A	0.396 (2)	0.586 (3)	0.4552 (6)	0.030 (5)*
H2B	0.310 (2)	0.479 (4)	0.4956 (5)	0.037 (5)*
H4A	−0.048 (2)	−0.199 (4)	0.4762 (5)	0.036 (5)*
H4B	−0.064 (2)	−0.335 (3)	0.4295 (5)	0.025 (4)*
H8	0.08592	−0.23356	0.30707	0.0300*
H9	0.11117	−0.25589	0.22782	0.0340*
H10	0.27259	0.04251	0.19139	0.0320*
H11	0.40825	0.36686	0.23422	0.0340*
H12	0.37871	0.39995	0.31324	0.0300*
H4C	0.644 (2)	1.126 (4)	0.4484 (8)	0.067 (8)*
H14A	0.62596	1.09709	0.34604	0.0270*
H14B	0.77172	0.91206	0.36249	0.0270*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0224 (7)	0.0195 (7)	0.0178 (6)	−0.0027 (5)	0.0021 (5)	−0.0005 (5)
N2	0.0268 (7)	0.0270 (7)	0.0178 (6)	−0.0097 (6)	0.0043 (5)	−0.0029 (5)
N3	0.0222 (7)	0.0228 (7)	0.0194 (6)	−0.0042 (5)	0.0025 (5)	−0.0007 (5)
N4	0.0277 (7)	0.0247 (7)	0.0212 (7)	−0.0077 (5)	0.0060 (5)	−0.0039 (6)
N5	0.0220 (6)	0.0209 (7)	0.0204 (6)	−0.0019 (5)	0.0028 (5)	−0.0014 (5)
O1	0.0295 (6)	0.0263 (6)	0.0257 (6)	−0.0094 (5)	0.0011 (5)	−0.0036 (5)
C2	0.0194 (7)	0.0205 (8)	0.0191 (7)	0.0009 (6)	0.0014 (6)	−0.0003 (6)
O2	0.0399 (7)	0.0292 (6)	0.0232 (6)	−0.0111 (5)	0.0093 (5)	−0.0025 (5)
O3	0.0296 (6)	0.0249 (6)	0.0273 (6)	−0.0074 (5)	0.0018 (5)	−0.0007 (4)
C4	0.0184 (7)	0.0192 (7)	0.0225 (7)	0.0015 (6)	0.0014 (6)	−0.0002 (6)
O4	0.0389 (7)	0.0234 (6)	0.0226 (6)	−0.0073 (5)	0.0057 (5)	−0.0052 (4)
C6	0.0172 (7)	0.0194 (7)	0.0207 (7)	0.0024 (6)	−0.0007 (6)	−0.0008 (6)
C7	0.0205 (7)	0.0208 (8)	0.0198 (7)	0.0029 (6)	−0.0007 (6)	0.0004 (6)
C8	0.0274 (8)	0.0238 (8)	0.0250 (8)	−0.0040 (6)	0.0018 (6)	−0.0020 (6)
C9	0.0340 (9)	0.0260 (9)	0.0251 (8)	−0.0016 (7)	−0.0033 (7)	−0.0063 (6)
C10	0.0329 (9)	0.0291 (9)	0.0183 (7)	0.0048 (7)	0.0006 (6)	−0.0006 (6)
C11	0.0347 (9)	0.0274 (9)	0.0221 (8)	−0.0028 (7)	0.0032 (7)	0.0023 (6)
C12	0.0290 (8)	0.0235 (8)	0.0217 (8)	−0.0037 (6)	−0.0005 (6)	−0.0013 (6)
C13	0.0210 (8)	0.0204 (8)	0.0228 (7)	0.0012 (6)	0.0007 (6)	0.0003 (6)
C14	0.0264 (8)	0.0230 (8)	0.0184 (7)	−0.0042 (6)	0.0015 (6)	−0.0004 (6)
C15	0.0221 (8)	0.0192 (8)	0.0212 (7)	0.0013 (6)	−0.0009 (6)	0.0010 (6)

Geometric parameters ($\text{\AA}$, $^\circ$)

N1—C2	1.3708 (19)	C6—C7	1.479 (2)
N1—C6	1.3651 (19)	C7—C8	1.398 (2)
N2—C2	1.314 (2)	C7—C12	1.389 (2)
N3—C2	1.3280 (19)	C8—C9	1.383 (2)
N3—C4	1.3443 (19)	C9—C10	1.381 (2)
N4—C4	1.317 (2)	C10—C11	1.381 (2)
N5—C4	1.3664 (19)	C11—C12	1.386 (2)
N5—C6	1.3008 (19)	O4—H4C	0.860 (19)
N1—H1	0.916 (19)	C8—H8	0.9500
O1—C13	1.2393 (19)	C9—H9	0.9500
N2—H2A	0.872 (16)	C10—H10	0.9500
O2—C13	1.2709 (19)	C11—H11	0.9500
N2—H2B	0.889 (15)	C12—H12	0.9500
O3—C15	1.2148 (19)	C13—C14	1.520 (2)
O4—C15	1.3131 (19)	C14—C15	1.512 (2)
N4—H4A	0.885 (15)	C14—H14A	0.9900
N4—H4B	0.876 (15)	C14—H14B	0.9900
C2—N1—C6	119.04 (12)	C10—C11—C12	120.37 (14)
C2—N3—C4	115.90 (12)	C7—C12—C11	120.10 (14)
C4—N5—C6	116.57 (12)	C15—O4—H4C	104.9 (15)

C6—N1—H1	122.8 (11)	C7—C8—H8	120.00
C2—N1—H1	118.1 (11)	C9—C8—H8	120.00
N1—C2—N3	121.36 (13)	C10—C9—H9	120.00
N1—C2—N2	118.26 (13)	C8—C9—H9	120.00
C2—N2—H2A	124.0 (11)	C11—C10—H10	120.00
C2—N2—H2B	117.5 (12)	C9—C10—H10	120.00
H2A—N2—H2B	118.5 (17)	C10—C11—H11	120.00
N2—C2—N3	120.38 (13)	C12—C11—H11	120.00
C4—N4—H4B	119.6 (10)	C7—C12—H12	120.00
H4A—N4—H4B	120.1 (16)	C11—C12—H12	120.00
C4—N4—H4A	119.9 (13)	O1—C13—C14	117.99 (13)
N3—C4—N4	118.66 (13)	O2—C13—C14	117.74 (13)
N3—C4—N5	125.26 (13)	O1—C13—O2	124.27 (14)
N4—C4—N5	116.07 (13)	C13—C14—C15	118.30 (12)
N1—C6—N5	121.63 (13)	O3—C15—C14	120.97 (13)
N1—C6—C7	119.64 (13)	O4—C15—C14	117.43 (13)
N5—C6—C7	118.73 (13)	O3—C15—O4	121.59 (14)
C6—C7—C12	123.13 (13)	C13—C14—H14A	108.00
C8—C7—C12	119.29 (13)	C13—C14—H14B	108.00
C6—C7—C8	117.57 (13)	C15—C14—H14A	108.00
C7—C8—C9	119.99 (14)	C15—C14—H14B	108.00
C8—C9—C10	120.42 (14)	H14A—C14—H14B	107.00
C9—C10—C11	119.83 (14)		
C6—N1—C2—N2	176.51 (14)	N5—C6—C7—C8	0.6 (2)
C6—N1—C2—N3	−3.7 (2)	N5—C6—C7—C12	179.60 (14)
C2—N1—C6—N5	−0.6 (2)	C6—C7—C8—C9	178.45 (14)
C2—N1—C6—C7	179.08 (13)	C12—C7—C8—C9	−0.6 (2)
C4—N3—C2—N1	3.9 (2)	C6—C7—C12—C11	−179.34 (14)
C4—N3—C2—N2	−176.35 (14)	C8—C7—C12—C11	−0.4 (2)
C2—N3—C4—N4	−179.31 (14)	C7—C8—C9—C10	0.9 (2)
C2—N3—C4—N5	0.0 (2)	C8—C9—C10—C11	−0.2 (2)
C6—N5—C4—N3	−4.0 (2)	C9—C10—C11—C12	−0.8 (2)
C6—N5—C4—N4	175.33 (14)	C10—C11—C12—C7	1.1 (2)
C4—N5—C6—N1	4.1 (2)	O1—C13—C14—C15	176.07 (13)
C4—N5—C6—C7	−175.56 (13)	O2—C13—C14—C15	−3.7 (2)
N1—C6—C7—C8	−179.06 (13)	C13—C14—C15—O3	178.49 (14)
N1—C6—C7—C12	−0.1 (2)	C13—C14—C15—O4	−1.1 (2)

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O1	0.916 (19)	1.877 (19)	2.7831 (16)	169.9 (16)
N2—H2A $\cdots$ O2	0.87 (2)	1.94 (2)	2.8100 (18)	174 (2)
N2—H2B $\cdots$ O4 ⁱ	0.89 (2)	2.21 (2)	2.9690 (17)	144 (2)
N4—H4A $\cdots$ N3 ⁱⁱ	0.89 (2)	2.13 (2)	3.0127 (19)	172 (2)
N4—H4B $\cdots$ O3 ⁱⁱⁱ	0.88 (2)	1.98 (2)	2.8514 (19)	175 (2)
O4—H4C $\cdots$ O2	0.86 (2)	1.63 (2)	2.4598 (16)	161 (2)

C8—H8···N5	0.95	2.42	2.7535 (19)	101
C10—H10···O3 ^{iv}	0.95	2.59	3.4305 (19)	147
C12—H12···O1	0.95	2.31	3.2425 (19)	166

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y, -z+1$; (iii) $x-1, y-2, z$; (iv) $-x+1, y-3/2, -z+1/2$.

2,4-Diamino-6-phenyl-1,3,5-triazin-ium 2,3-bis(benzoyloxy)-3-carboxypropanoate (III)

Crystal data

$C_9H_{10}N_5^+ \cdot C_{18}H_{13}O_8^-$

$M_r = 545.50$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_yb$

$a = 11.2689\ (6)\ \text{\AA}$

$b = 7.6863\ (3)\ \text{\AA}$

$c = 15.0741\ (7)\ \text{\AA}$

$\beta = 100.194\ (2)^\circ$

$V = 1285.05\ (10)\ \text{\AA}^3$

$Z = 2$

$F(000) = 568$

$D_x = 1.410\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4512 reflections

$\theta = 1.8\text{--}25.0^\circ$

$\mu = 0.11\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Block, colourless

$0.24 \times 0.16 \times 0.13\ \text{mm}$

Data collection

Bruker APEX IV CCD

diffractometer

Radiation source: microfocus sealed X-ray tube

Mirror optics monochromator

φ and ω scans

22302 measured reflections

4512 independent reflections

4282 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 1.8^\circ$

$h = -13 \rightarrow 13$

$k = -9 \rightarrow 9$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.077$

$S = 1.09$

4512 reflections

385 parameters

8 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$W = 1/[\Sigma^2(FO^2) + (0.0329P)^2 + 0.1322P]$

WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.12\ \text{e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.22\ \text{e \AA}^{-3}$

Absolute structure: Flack (1983)

Absolute structure parameter: 0.500

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors.

Weighted R-factors wR and all goodnesses of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating $-R$ -factor-obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.61976 (15)	0.7242 (2)	0.82282 (11)	0.0311 (5)

O2	0.81424 (14)	0.6576 (2)	0.87266 (11)	0.0301 (5)
O3	0.79253 (16)	0.0758 (2)	0.90975 (11)	0.0354 (6)
O4	0.65478 (17)	0.0309 (2)	0.78551 (12)	0.0361 (6)
O5	0.54806 (14)	0.3931 (2)	0.83443 (10)	0.0267 (5)
O6	0.50458 (16)	0.4518 (3)	0.97104 (11)	0.0382 (6)
O7	0.69196 (15)	0.3423 (2)	0.71769 (10)	0.0276 (5)
O8	0.83737 (15)	0.1733 (2)	0.67966 (12)	0.0373 (6)
C13	0.7049 (2)	0.6222 (3)	0.85174 (15)	0.0249 (7)
C14	0.6734 (2)	0.4307 (3)	0.86497 (15)	0.0249 (7)
C15	0.7421 (2)	0.3128 (3)	0.81074 (15)	0.0256 (7)
C16	0.7318 (2)	0.1239 (3)	0.83900 (16)	0.0277 (7)
C17	0.4733 (2)	0.4019 (3)	0.89478 (15)	0.0271 (7)
C18	0.3502 (2)	0.3462 (3)	0.85424 (16)	0.0283 (7)
C19	0.2571 (2)	0.3748 (4)	0.90205 (18)	0.0375 (8)
C20	0.1413 (2)	0.3273 (4)	0.8648 (2)	0.0447 (9)
C21	0.1162 (3)	0.2474 (4)	0.7817 (2)	0.0466 (10)
C22	0.2091 (3)	0.2150 (5)	0.73538 (19)	0.0485 (10)
C23	0.3257 (2)	0.2652 (4)	0.77043 (17)	0.0392 (9)
C24	0.7462 (2)	0.2569 (3)	0.65784 (16)	0.0283 (7)
C25	0.6802 (2)	0.2762 (3)	0.56458 (16)	0.0302 (7)
C26	0.5797 (2)	0.3830 (4)	0.54361 (17)	0.0360 (8)
C27	0.5227 (3)	0.3997 (5)	0.45508 (19)	0.0471 (9)
C28	0.5625 (3)	0.3074 (5)	0.3878 (2)	0.0563 (13)
C29	0.6615 (3)	0.1990 (5)	0.4085 (2)	0.0557 (13)
C30	0.7208 (2)	0.1844 (4)	0.49649 (18)	0.0403 (9)
N1	1.01637 (19)	0.8228 (3)	0.83650 (13)	0.0313 (6)
N2	1.0355 (2)	0.9683 (3)	0.97223 (15)	0.0357 (7)
N3	1.20669 (18)	0.8942 (3)	0.91848 (13)	0.0313 (6)
N4	1.37005 (19)	0.8116 (3)	0.85938 (15)	0.0362 (7)
N5	1.18506 (19)	0.7588 (3)	0.77252 (14)	0.0335 (6)
C2	1.0882 (2)	0.8964 (3)	0.90968 (15)	0.0292 (7)
C4	1.2519 (2)	0.8211 (3)	0.85098 (16)	0.0303 (7)
C6	1.0684 (2)	0.7616 (3)	0.76770 (16)	0.0307 (7)
C7	0.9888 (2)	0.7008 (3)	0.68514 (16)	0.0327 (7)
C8	1.0345 (3)	0.5868 (4)	0.62804 (18)	0.0422 (9)
C9	0.9626 (3)	0.5338 (5)	0.54803 (19)	0.0500 (11)
C10	0.8464 (3)	0.5960 (4)	0.52476 (19)	0.0483 (10)
C11	0.8011 (3)	0.7089 (4)	0.5814 (2)	0.0489 (10)
C12	0.8715 (3)	0.7618 (4)	0.66202 (19)	0.0405 (8)
H4C	0.649 (4)	−0.073 (3)	0.806 (3)	0.086 (14)*
H14	0.69557	0.40040	0.93032	0.0300*
H15	0.82901	0.34740	0.82192	0.0310*
H19	0.27340	0.42689	0.96009	0.0450*
H20	0.07755	0.34979	0.89690	0.0540*
H21	0.03587	0.21503	0.75655	0.0560*
H22	0.19275	0.15748	0.67875	0.0580*
H23	0.38884	0.24445	0.73751	0.0470*
H26	0.55028	0.44427	0.58999	0.0430*

H27	0.45547	0.47556	0.44049	0.0570*
H28	0.52193	0.31808	0.32722	0.0670*
H29	0.68867	0.13468	0.36215	0.0670*
H30	0.78956	0.11127	0.51049	0.0480*
H1	0.938 (3)	0.800 (4)	0.8390 (19)	0.045 (8)*
H2A	0.958 (2)	0.999 (4)	0.9604 (18)	0.041 (8)*
H2B	1.080 (3)	1.022 (4)	1.0196 (17)	0.049 (9)*
H4A	1.417 (3)	0.849 (4)	0.9098 (16)	0.050 (9)*
H4B	1.400 (3)	0.763 (4)	0.8164 (17)	0.042 (8)*
H8	1.11483	0.54502	0.64371	0.0510*
H9	0.99353	0.45472	0.50933	0.0600*
H10	0.79769	0.56095	0.46967	0.0580*
H11	0.72094	0.75093	0.56522	0.0590*
H12	0.83952	0.83905	0.70100	0.0490*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0251 (9)	0.0254 (9)	0.0407 (9)	−0.0004 (7)	0.0004 (7)	0.0042 (7)
O2	0.0213 (8)	0.0279 (9)	0.0400 (9)	−0.0049 (7)	0.0027 (7)	0.0010 (7)
O3	0.0354 (11)	0.0312 (9)	0.0358 (9)	0.0042 (8)	−0.0038 (8)	0.0057 (7)
O4	0.0371 (11)	0.0259 (9)	0.0406 (10)	−0.0069 (8)	−0.0058 (8)	0.0062 (8)
O5	0.0207 (8)	0.0299 (8)	0.0289 (8)	−0.0051 (7)	0.0029 (6)	0.0001 (7)
O6	0.0301 (10)	0.0539 (12)	0.0290 (9)	0.0019 (8)	0.0010 (7)	−0.0058 (8)
O7	0.0282 (9)	0.0266 (9)	0.0278 (8)	0.0021 (7)	0.0047 (6)	0.0023 (7)
O8	0.0272 (9)	0.0426 (11)	0.0407 (10)	0.0067 (8)	0.0026 (8)	−0.0027 (8)
C13	0.0237 (12)	0.0268 (12)	0.0238 (11)	−0.0016 (10)	0.0032 (9)	−0.0001 (9)
C14	0.0176 (11)	0.0280 (13)	0.0277 (11)	−0.0032 (9)	0.0004 (9)	0.0023 (9)
C15	0.0205 (11)	0.0269 (12)	0.0281 (11)	−0.0028 (10)	0.0007 (9)	0.0033 (10)
C16	0.0246 (12)	0.0267 (12)	0.0310 (12)	0.0007 (10)	0.0028 (10)	0.0011 (10)
C17	0.0247 (12)	0.0265 (11)	0.0301 (12)	0.0019 (10)	0.0047 (9)	0.0022 (10)
C18	0.0223 (12)	0.0299 (13)	0.0325 (12)	0.0007 (10)	0.0045 (9)	0.0023 (10)
C19	0.0292 (14)	0.0430 (15)	0.0413 (14)	−0.0008 (12)	0.0093 (11)	−0.0033 (12)
C20	0.0258 (14)	0.0527 (17)	0.0583 (17)	0.0018 (13)	0.0145 (12)	0.0022 (15)
C21	0.0260 (14)	0.0562 (19)	0.0548 (17)	−0.0087 (13)	−0.0005 (13)	0.0076 (15)
C22	0.0356 (15)	0.070 (2)	0.0375 (14)	−0.0156 (15)	0.0002 (12)	−0.0077 (14)
C23	0.0309 (14)	0.0533 (17)	0.0340 (13)	−0.0067 (12)	0.0078 (11)	−0.0063 (12)
C24	0.0249 (13)	0.0250 (12)	0.0360 (13)	−0.0034 (10)	0.0082 (10)	0.0002 (10)
C25	0.0268 (13)	0.0312 (13)	0.0334 (12)	−0.0046 (10)	0.0074 (10)	0.0026 (10)
C26	0.0313 (14)	0.0387 (14)	0.0381 (13)	0.0021 (12)	0.0063 (11)	0.0018 (11)
C27	0.0370 (16)	0.0569 (18)	0.0448 (15)	0.0094 (15)	0.0001 (12)	0.0073 (15)
C28	0.0426 (18)	0.090 (3)	0.0345 (14)	0.0090 (17)	0.0018 (12)	0.0050 (16)
C29	0.0463 (18)	0.088 (3)	0.0337 (14)	0.0099 (18)	0.0095 (13)	−0.0073 (16)
C30	0.0314 (14)	0.0525 (17)	0.0378 (14)	0.0047 (13)	0.0087 (11)	0.0012 (13)
N1	0.0215 (11)	0.0404 (12)	0.0316 (10)	−0.0048 (9)	0.0037 (8)	0.0014 (9)
N2	0.0225 (12)	0.0518 (14)	0.0324 (11)	0.0026 (10)	0.0042 (9)	−0.0031 (10)
N3	0.0229 (11)	0.0399 (11)	0.0303 (10)	−0.0013 (9)	0.0029 (8)	−0.0001 (9)
N4	0.0230 (11)	0.0504 (14)	0.0356 (12)	−0.0014 (10)	0.0063 (9)	−0.0083 (11)

N5	0.0268 (11)	0.0412 (12)	0.0319 (10)	−0.0039 (9)	0.0039 (8)	−0.0028 (9)
C2	0.0253 (13)	0.0339 (12)	0.0280 (11)	−0.0025 (11)	0.0035 (9)	0.0045 (10)
C4	0.0260 (13)	0.0338 (12)	0.0309 (12)	−0.0018 (10)	0.0049 (10)	0.0015 (11)
C6	0.0280 (13)	0.0317 (13)	0.0319 (12)	−0.0031 (10)	0.0041 (10)	0.0022 (10)
C7	0.0307 (13)	0.0343 (13)	0.0324 (12)	−0.0105 (11)	0.0041 (10)	0.0031 (10)
C8	0.0334 (15)	0.0528 (17)	0.0408 (14)	−0.0116 (13)	0.0076 (12)	−0.0070 (13)
C9	0.051 (2)	0.062 (2)	0.0388 (15)	−0.0224 (16)	0.0128 (14)	−0.0131 (15)
C10	0.0521 (19)	0.0581 (19)	0.0310 (13)	−0.0266 (16)	−0.0028 (13)	0.0046 (13)
C11	0.0413 (16)	0.0512 (18)	0.0477 (16)	−0.0082 (14)	−0.0099 (13)	0.0088 (14)
C12	0.0367 (15)	0.0376 (14)	0.0436 (14)	−0.0022 (12)	−0.0026 (12)	0.0026 (12)

Geometric parameters (Å, °)

O1—C13	1.256 (3)	N4—C4	1.317 (3)
O2—C13	1.247 (3)	N5—C4	1.371 (3)
O3—C16	1.218 (3)	N5—C6	1.304 (3)
O4—C16	1.291 (3)	C14—H14	1.0000
O5—C14	1.435 (3)	C15—H15	1.0000
O5—C17	1.347 (3)	C19—H19	0.9500
O6—C17	1.204 (3)	C20—H20	0.9500
O7—C15	1.434 (3)	C21—H21	0.9500
O7—C24	1.347 (3)	C22—H22	0.9500
O8—C24	1.207 (3)	C23—H23	0.9500
O4—H4C	0.86 (3)	C26—H26	0.9500
C13—C14	1.535 (3)	C27—H27	0.9500
C14—C15	1.521 (3)	C28—H28	0.9500
C15—C16	1.523 (3)	C29—H29	0.9500
C17—C18	1.477 (3)	C30—H30	0.9500
C18—C23	1.392 (4)	N1—H1	0.91 (3)
C18—C19	1.391 (3)	N2—H2A	0.89 (2)
C19—C20	1.376 (3)	N2—H2B	0.90 (3)
C20—C21	1.379 (4)	N4—H4A	0.89 (3)
C21—C22	1.380 (5)	N4—H4B	0.87 (3)
C22—C23	1.382 (4)	C6—C7	1.475 (3)
C24—C25	1.477 (3)	C7—C8	1.390 (4)
C25—C30	1.388 (4)	C7—C12	1.388 (4)
C25—C26	1.389 (3)	C8—C9	1.390 (4)
C26—C27	1.381 (4)	C9—C10	1.380 (5)
C27—C28	1.376 (5)	C10—C11	1.377 (4)
C28—C29	1.383 (5)	C11—C12	1.389 (4)
C29—C30	1.380 (4)	C8—H8	0.9500
N1—C6	1.362 (3)	C9—H9	0.9500
N1—C2	1.370 (3)	C10—H10	0.9500
N2—C2	1.321 (3)	C11—H11	0.9500
N3—C4	1.339 (3)	C12—H12	0.9500
N3—C2	1.318 (3)		
C14—O5—C17	118.10 (17)	C22—C21—H21	120.00

C15—O7—C24	115.54 (18)	C23—C22—H22	120.00
C16—O4—H4C	112 (3)	C21—C22—H22	120.00
O1—C13—C14	117.6 (2)	C22—C23—H23	120.00
O2—C13—C14	114.7 (2)	C18—C23—H23	120.00
O1—C13—O2	127.7 (2)	C25—C26—H26	120.00
O5—C14—C15	105.86 (18)	C27—C26—H26	120.00
C13—C14—C15	110.49 (18)	C26—C27—H27	120.00
O5—C14—C13	112.85 (18)	C28—C27—H27	120.00
O7—C15—C16	112.82 (18)	C29—C28—H28	120.00
C14—C15—C16	110.27 (19)	C27—C28—H28	120.00
O7—C15—C14	106.35 (18)	C28—C29—H29	120.00
O3—C16—C15	118.4 (2)	C30—C29—H29	120.00
O4—C16—C15	115.4 (2)	C25—C30—H30	120.00
O3—C16—O4	126.2 (2)	C29—C30—H30	120.00
O5—C17—C18	111.10 (19)	C6—N1—H1	121.2 (18)
O6—C17—C18	125.6 (2)	C2—N1—H1	119.1 (18)
O5—C17—O6	123.3 (2)	N1—C2—N3	121.3 (2)
C17—C18—C19	118.6 (2)	N1—C2—N2	118.1 (2)
C19—C18—C23	119.6 (2)	C2—N2—H2A	121.1 (18)
C17—C18—C23	121.8 (2)	C2—N2—H2B	120 (2)
C18—C19—C20	119.6 (2)	H2A—N2—H2B	115 (3)
C19—C20—C21	121.1 (3)	N2—C2—N3	120.6 (2)
C20—C21—C22	119.2 (3)	C4—N4—H4B	118 (2)
C21—C22—C23	120.8 (3)	H4A—N4—H4B	122 (3)
C18—C23—C22	119.6 (2)	C4—N4—H4A	120 (2)
O7—C24—O8	122.8 (2)	N3—C4—N4	117.7 (2)
O8—C24—C25	125.0 (2)	N3—C4—N5	125.2 (2)
O7—C24—C25	112.14 (19)	N4—C4—N5	117.1 (2)
C24—C25—C26	121.9 (2)	N1—C6—N5	121.9 (2)
C26—C25—C30	119.6 (2)	N1—C6—C7	118.2 (2)
C24—C25—C30	118.5 (2)	N5—C6—C7	119.9 (2)
C25—C26—C27	119.7 (3)	C6—C7—C12	121.0 (2)
C26—C27—C28	120.5 (3)	C8—C7—C12	119.9 (2)
C27—C28—C29	120.0 (3)	C6—C7—C8	119.1 (2)
C28—C29—C30	120.0 (3)	C7—C8—C9	120.0 (3)
C25—C30—C29	120.2 (3)	C8—C9—C10	120.0 (3)
C2—N1—C6	118.9 (2)	C9—C10—C11	120.0 (3)
C2—N3—C4	116.3 (2)	C10—C11—C12	120.7 (3)
C4—N5—C6	115.9 (2)	C7—C12—C11	119.5 (3)
O5—C14—H14	109.00	C7—C8—H8	120.00
C13—C14—H14	109.00	C9—C8—H8	120.00
C15—C14—H14	109.00	C8—C9—H9	120.00
O7—C15—H15	109.00	C10—C9—H9	120.00
C14—C15—H15	109.00	C9—C10—H10	120.00
C16—C15—H15	109.00	C11—C10—H10	120.00
C20—C19—H19	120.00	C10—C11—H11	120.00
C18—C19—H19	120.00	C12—C11—H11	120.00
C19—C20—H20	119.00	C7—C12—H12	120.00

C21—C20—H20	119.00	C11—C12—H12	120.00
C20—C21—H21	120.00		
C17—O5—C14—C13	−93.1 (2)	O8—C24—C25—C26	−176.1 (2)
C17—O5—C14—C15	145.97 (19)	O8—C24—C25—C30	3.9 (4)
C14—O5—C17—O6	5.6 (3)	C24—C25—C26—C27	178.6 (3)
C14—O5—C17—C18	−175.50 (18)	C30—C25—C26—C27	−1.4 (4)
C24—O7—C15—C14	176.06 (18)	C24—C25—C30—C29	180.0 (3)
C24—O7—C15—C16	−62.9 (2)	C26—C25—C30—C29	−0.1 (4)
C15—O7—C24—O8	−6.4 (3)	C25—C26—C27—C28	1.9 (5)
C15—O7—C24—C25	172.71 (18)	C26—C27—C28—C29	−1.0 (5)
O1—C13—C14—O5	4.8 (3)	C27—C28—C29—C30	−0.5 (5)
O1—C13—C14—C15	123.1 (2)	C28—C29—C30—C25	1.0 (5)
O2—C13—C14—O5	−176.04 (18)	C6—N1—C2—N2	174.4 (2)
O2—C13—C14—C15	−57.7 (3)	C6—N1—C2—N3	−6.5 (4)
O5—C14—C15—O7	53.1 (2)	C2—N1—C6—N5	5.4 (4)
O5—C14—C15—C16	−69.5 (2)	C2—N1—C6—C7	−173.3 (2)
C13—C14—C15—O7	−69.4 (2)	C4—N3—C2—N1	1.9 (3)
C13—C14—C15—C16	168.02 (18)	C4—N3—C2—N2	−178.9 (2)
O7—C15—C16—O3	164.8 (2)	C2—N3—C4—N4	−177.7 (2)
O7—C15—C16—O4	−17.4 (3)	C2—N3—C4—N5	4.0 (4)
C14—C15—C16—O3	−76.4 (3)	C6—N5—C4—N3	−5.0 (4)
C14—C15—C16—O4	101.4 (2)	C6—N5—C4—N4	176.7 (2)
O5—C17—C18—C19	−169.3 (2)	C4—N5—C6—N1	0.0 (4)
O5—C17—C18—C23	11.3 (3)	C4—N5—C6—C7	178.7 (2)
O6—C17—C18—C19	9.6 (4)	N1—C6—C7—C8	−158.4 (2)
O6—C17—C18—C23	−169.9 (3)	N1—C6—C7—C12	24.5 (3)
C17—C18—C19—C20	178.7 (3)	N5—C6—C7—C8	22.9 (4)
C23—C18—C19—C20	−1.9 (4)	N5—C6—C7—C12	−154.2 (3)
C17—C18—C23—C22	179.8 (3)	C6—C7—C8—C9	−177.3 (3)
C19—C18—C23—C22	0.4 (4)	C12—C7—C8—C9	−0.2 (4)
C18—C19—C20—C21	1.7 (5)	C6—C7—C12—C11	176.6 (3)
C19—C20—C21—C22	−0.1 (5)	C8—C7—C12—C11	−0.5 (4)
C20—C21—C22—C23	−1.5 (5)	C7—C8—C9—C10	0.8 (5)
C21—C22—C23—C18	1.3 (5)	C8—C9—C10—C11	−0.8 (5)
O7—C24—C25—C26	4.8 (3)	C9—C10—C11—C12	0.2 (5)
O7—C24—C25—C30	−175.3 (2)	C10—C11—C12—C7	0.4 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O2	0.91 (3)	1.91 (3)	2.745 (3)	152 (3)
N2—H2 <i>A</i> $\cdots$ O3 ⁱ	0.89 (2)	1.98 (2)	2.856 (3)	169 (2)
N2—H2 <i>B</i> $\cdots$ O2 ⁱⁱ	0.90 (3)	2.11 (3)	3.008 (3)	178 (2)
N4—H4 <i>A</i> $\cdots$ O6 ⁱⁱ	0.89 (3)	2.02 (3)	2.901 (3)	170 (3)
N4—H4 <i>B</i> $\cdots$ O1 ⁱⁱⁱ	0.87 (3)	2.48 (3)	3.037 (3)	123 (2)
O4—H4 <i>C</i> $\cdots$ O1 ^{iv}	0.86 (3)	1.62 (3)	2.471 (2)	167 (5)
C12—H12 $\cdots$ O8 ⁱ	0.95	2.59	3.203 (3)	123

C14—H14···N3 ^v	1.00	2.35	3.317 (3)	162
C15—H15···O2	1.00	2.52	2.879 (3)	101
C19—H19···O3 ^{vi}	0.95	2.50	3.363 (3)	152
C21—H21···O8 ^{vii}	0.95	2.35	3.294 (4)	171

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+2, y+1/2, -z+2$; (iii) $x+1, y, z$; (iv) $x, y-1, z$; (v) $-x+2, y-1/2, -z+2$; (vi) $-x+1, y+1/2, -z+2$; (vii) $x-1, y, z$.