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Salts of 3,5-dinitrobenzoic acid with organic diamines: hydrogen-bonded supramolecular structures in one, two and three dimensions

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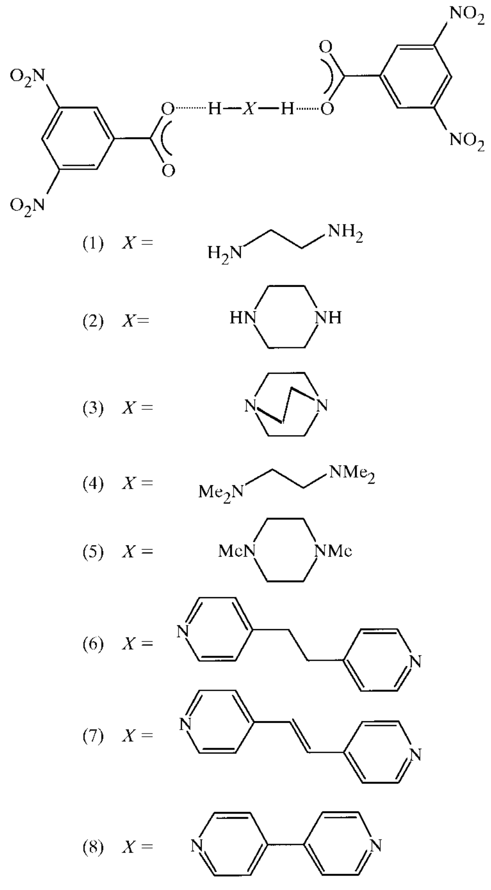
The trigonally trisubstituted carboxylic acid 3,5-dinitrobenzoic acid, $(O_2N)_2C_6H_3COOH$, forms 2:1 salts with a range of organic diamines L, with the general composition $[LH_2]^{2+}\cdot[\{(O_2N)_2C_6H_3COO\}^-]_2$. When L is a bis-tertiary amine the hard N—H···O hydrogen bonds generate finite three-component aggregates, anion···cation···anion, and these aggregates are further linked by soft C—H···O hydrogen bonds to form one-dimensional molecular ladders when L is N,N,N',N''-tetramethyl-1,2-diaminoethane and chains of rings when L is 4,4′-dipyridylethane or 4,4′-dipyridylethene; two-dimensional sheets are formed when L is 1,4-diazabicyclo[2.2.2]octane and a three-dimensional framework is formed when L is N,N'-dimethylpiperazine. When L is the bis-secondary amine piperazine, the hard N—H···O and soft C—H···O hydrogen bonds each generate continuous motifs in the form of distinct chains of rings, the combination of which generates sheets, while when L is the bis-primary amine 1,2-diaminoethane the hard N—H···O hydrogen bonds alone generate a three-dimensional framework.

1. Introduction

Carboxylic acids when co-crystallized with organic amines generally form salts in which there is complete, or occasionally only partial, transfer of protons from the acid to the base. Thus, with such bases the trigonally trisubstituted acid 3,5-dinitrobenzoic acid, $(O_2N)_2C_6H_3COOH$, is expected to form the anion $[(O_2N)_2C_6H_3COO]^-$: this has approximate $D_{3h}(\bar{6}m2)$ symmetry and can act as a multiple acceptor of hydrogen bonds where the acceptor groups $-NO_2$ and $-CO_2^-$ are all carried on a rigid planar framework. We have now initiated a systematic study of the crystal structures of hydrogen-bonded salts formed by this acid with polyamines, and report here the structures of seven such compounds (1)–(7) formed by diamines.

For the diamine components in (1)–(5) the common feature is the N—C—C—N linkage containing two N atoms, capable of acting either as hydrogen-bond acceptors or as proton acceptors and thence as hydrogen-bond donors, which are separated by a two-atom linked unit. The diamines forming (3), (2) and (1) are respectively tertiary, secondary and primary amines, expected when protonated to form an increasingly complex range of N—H···O hydrogen bonds: the diamines forming (4) and (5) have the same skeletons as those in (1) and (2), respectively, but both are tertiary amines. Thus, the diamines in (3), (5) and (4) form another series of tertiary amines which are respectively bicyclic, monocyclic and acyclic.

The diamines in (6)–(8) are all 4,4′-bipyridyls, having different spacer units (or none) between the heteroaromatic rings.



2. Experimental

2.1. Syntheses

Stoichiometric quantities of 3,5-dinitrobenzoic acid and the appropriate diamine were separately dissolved in methanol. These solutions were mixed to give, in every case, a molar ratio of acid-to-base of 2:1; the resulting mixtures were then set aside to crystallize, exposed to the laboratory atmosphere, producing analytically pure samples of (1)–(8). Analyses: (1), found C 39.9, H 3.1, N 17.3%; $C_{16}H_{16}N_6O_{12}$ requires C 39.7, H 3.3, N 17.4%; (2), found C 42.6, H 3.4, N 15.9%; $C_{18}H_{18}N_6O_{12}$ requires C 42.4, H 3.6, N 16.5%; (3), found C 44.7, H 3.7, N 15.6%; $C_{20}H_{20}N_6O_{12}$ requires C 44.8, H 3.8, N 15.7%; $C_{20}H_{20}N_6O_{12}.0.13H_2O$ requires C 44.6, H 3.8, N 15.6%; (4), found C 44.8, H 4.3, N 15.2%; $C_{20}H_{24}N_6O_{12}$ requires C 44.4, H 4.5, N 15.5%; (5), found C 44.7, H 4.0, N 15.6%; $C_{20}H_{22}N_6O_{12}$ requires C 44.6, H 4.1, N 15.6%; (6), found C 51.1, H 3.2, N 13.7%; $C_{26}H_{20}N_6O_{12}$ requires C 51.3, H 3.3, N 13.8%; (7), found C 51.4, H 2.8, N 13.8%; $C_{26}H_{18}N_6O_{12}$ requires C 51.5, H 3.0, N 13.9%; (8), found C 49.5, H 2.5, N 14.3%; $C_{24}H_{16}N_6O_{12}$ requires C 49.7, H 2.8, N 14.5%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

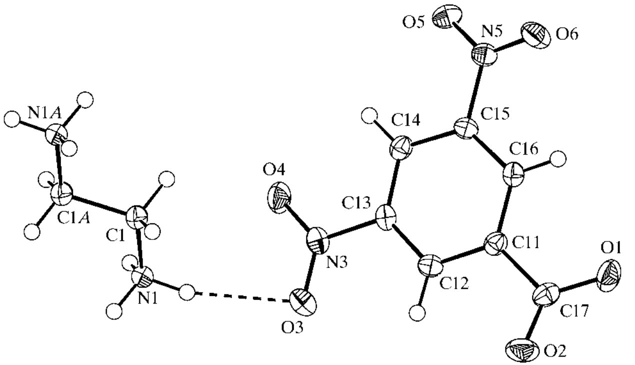


Figure 1
The molecular components of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked *A* are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

2.2. Data collection, structure solution and refinement

Diffraction data for (1)–(8) were collected at 150 (2) K using a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized for (1)–(7) in Table 1, together with details of the software employed (Ferguson, 1999; Gabe *et al.*, 1989; Johnson, 1976; Nonius, 1997; Otwinowski & Minor, 1997; Sheldrick, 1997*a*,*b*; Spek, 2000). For (1) and (3)–(6), the space group $P2_1/c$ was uniquely assigned from the systematic absences. Compounds (2) and (7) are triclinic: the space group $P\bar{1}$ was assumed, and confirmed by the structure analysis. The structures of (1)–(7) were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical

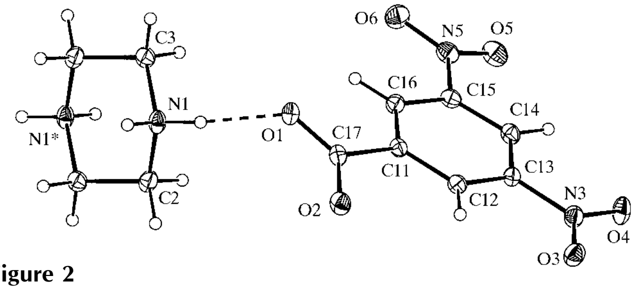


Figure 2
The molecular components of (2), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atom marked with a star (*) is at the symmetry position $(1 - x, 1 - y, 1 - z)$.

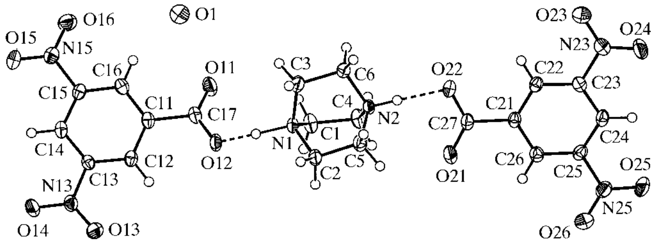


Figure 3
The molecular components of (3), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms associated with the partially occupied site O1 could not be located (see text).

bias (Wilson, 1976). All H atoms were located from difference maps, and all were included in the refinements as riding atoms with O—H 0.84, N—H 0.88–0.93, C—H 0.95 (aromatic and aliphatic ═CH—), 0.98 (CH_3), 0.99 Å (CH_2). In (1), (2), (4) and (5) there is complete transfer of one proton from each molecule of the acid to the base yielding dications, and in all these compounds the H atoms are all fully ordered. In (3) one of the transferred H atoms (H2) has been transferred fully to N2, but the other (H1) is located almost mid-way between N1 and O12, although it is marginally closer to N1 (Table 2): it was not possible to locate the H atoms for the partial water molecule. In (6) the proton between O1 and N1 occupies two sites with equal occupancy, one (H1) adjacent to O1 and the other (H1*A*) adjacent to N1: in (7) there is a single H site almost exactly centred between N11 and O1. For (8) the diffraction data from a number of crystals could always be indexed in terms of a monoclinic cell, a = 5.8970 (3), b = 22.8849 (10), c = 9.3297 (4) Å, β = 101.064 (3)°, consistent with the presence of four acid and two bipyridyl units in the unit cell. Although the data exhibited no systematic absences, structure solution was not possible in space groups *P*2, *Pm* or *P*2/*m*, but could be achieved readily in either $P2_1$ or $P2_1/m$; however, in neither case could the structure be refined below R = 0.14.

The diagrams were prepared with the aid of *PLATON* (Spek, 2000). Hydrogen-bond dimensions are presented in Table 2.[1] Figs. 1–7 show the molecular components, with the atom-labelling schemes. Figs. 8–20 illustrate aspects of the supramolecular structures.

3. Results and discussion

3.1. Molecular constitutions

Each of (1)–(8) contains a 2:1 ratio of dinitrobenzoic acid to the diamine base. Compound (3) is, in addition, partially hydrated: the water site is only partially occupied, with site occupation factor 0.130 (5). It was not possible to diagnose the presence of this partial hydration from the elemental analysis. While proton transfer from acid to diamine is complete in (1), (2), (4) and (5), it is incomplete in (3), (6) and (7) (see §2.2). Subject to these provisos, all of the compounds (1)–(7) whose structures are reported here have the general formula $[LH_2]^{2+}\cdot[\{(O_2N)_2C_6H_3COO\}^-]_2$, where L in each case represents the neutral diamine (see Scheme I). While we have been unable to refine the structure of (8) its composition suggests that its constitution may resemble those of (6) and (7).

3.2. Supramolecular structures

Within the asymmetric units (Figs. 1–7) the ionic components are linked by N—H···O hydrogen bonds (Table 2). In compounds derived from bis-tertiary amines, there are just two hard (Braga *et al.*, 1995) hydrogen bonds, linking the ionic components into a finite (zero-dimensional) aggregate, anion–cation–anion, but soft (Braga *et al.*, 1995) hydrogen bonds of C—H···O-type may link the finite aggregates into continuous arrays in one, two or three dimensions. Where the amine is of bis-secondary or bis-primary type there will be four or six N—H bonds in the cation, permitting the development of continuous hydrogen-bonded arrays generated by hard hydrogen bonds. It is convenient to classify the structures under consideration here firstly in terms of the dimensionality of the supramolecular arrays generated by the hard hydrogen bonds, and secondly in terms of the corresponding effects of the soft hydrogen bonds.

3.2.1. Hard hydrogen bonds generate finite aggregates. In (3)–(7) the hard hydrogen bonds generate finite three-component aggregates: soft C—H···O hydrogen bonds generate one-dimensional arrays in (4), (6) and (7), a two-dimensional sheet in (3) and a three-dimensional framework in (5); it is convenient to discuss these different dimensionalities separately.

Soft hydrogen bonds generate one-dimensional arrays: In (4) the cation $[HMe_2NCH_2CH_2NMe_2H]^{2+}$ lies across a centre of inversion, chosen for convenience as that at the centre of

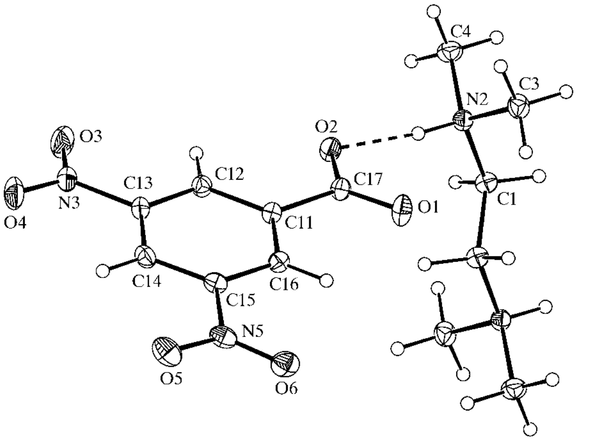


Figure 4
The molecular components of (4), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

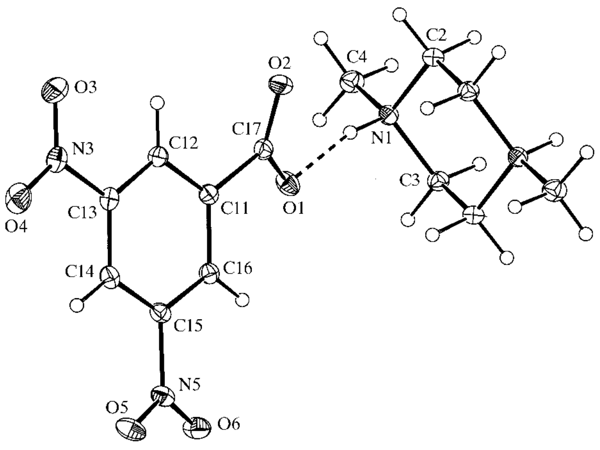


Figure 5
The molecular components of (5), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0113). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$2(C_7H_3N_2O_6)\cdot C_2H_{10}N_2$	$2(C_7H_3N_2O_6)\cdot C_4H_{12}N_2$	$C_6H_{13}N_2\cdot C_7H_4N_2O_6\cdot C_7H_3N_2O_6\cdot 0.13H_2O$	$2(C_7H_3N_2O_6)\cdot C_6H_{18}N_2$	$2(C_7H_3N_2O_6)\cdot C_6H_{16}N_2$
Chemical formula weight	484.35	510.38	538.78	540.45	538.44
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	5.4549 (2), 10.6869 (4), 17.4420 (6)	6.6970 (5), 9.1655 (8), 10.5942 (9)	11.6228 (4), 10.4320 (3), 19.6350 (6)	6.0665 (2), 9.0635 (3), 21.8452 (6)	7.1399 (2), 21.1749 (6), 7.8255 (2)
α, β, γ (°)	90, 95.704 (2), 90	65.338 (3), 85.985 (4), 69.313 (3)	90, 109.6890 (18), 90	90, 92.031 (2), 90	90, 99.1990 (18), 90
V (Å^3)	1011.76 (6)	550.57 (8)	2241.54 (12)	1200.38 (7)	1167.90 (6)
Z	2	1	4	2	2
D_x (Mg m^{-3})	1.590	1.539	1.597	1.495	1.531
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	8774	2481	5110	4055	3926
θ range (°)	3.02–27.49	2.59–27.51	2.67–27.49	2.92–32.05	2.81–32.01
μ (mm^{-1})	0.139	0.132	0.134	0.125	0.129
Temperature (K)	150 (2)	100.0 (1)	100.0 (1)	100.0 (1)	100.0 (1)
Crystal form, colour	Block, colourless	Block, colourless	Plate, colourless	Block, colourless	Block, colourless
Crystal size (mm)	0.26 × 0.23 × 0.16	0.17 × 0.13 × 0.08	0.32 × 0.28 × 0.18	0.35 × 0.28 × 0.24	0.37 × 0.35 × 0.30
Data collection					
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
$T_{\min}$	0.9648	0.9779	0.9584	0.9574	0.9539
$T_{\max}$	0.9782	0.9895	0.9763	0.9705	0.9624
No. of measured, independent and observed parameters	8774, 2309, 1919	2481, 2481, 1725	5395, 5110, 3867	4055, 4055, 3109	4083, 3926, 3018
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.023	0.029	0.020	0.032	0.030
$\theta_{\max}$ (°)	27.49	27.51	27.49	32.05	32.01
Range of h, k, l	$0 \rightarrow h \rightarrow 7$ $0 \rightarrow k \rightarrow 13$ $-22 \rightarrow l \rightarrow 22$	$0 \rightarrow h \rightarrow 8$ $-10 \rightarrow k \rightarrow 11$ $-13 \rightarrow l \rightarrow 13$	$0 \rightarrow h \rightarrow 15$ $-13 \rightarrow k \rightarrow 0$ $-25 \rightarrow l \rightarrow 23$	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 13$ $-32 \rightarrow l \rightarrow 32$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 31$ $-11 \rightarrow l \rightarrow 11$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0393, 0.1196, 1.086	0.046, 0.1103, 1.045	0.0427, 0.1078, 1.054	0.0506, 0.1647, 1.123	0.0442, 0.1266, 1.075
No. of reflections and parameters used in refinement	2309, 156	2481, 164	5110, 348	4055, 175	3926, 174
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.3986P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.0563P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0450P)^2 + 0.6423P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.6243P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.4394P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.000	0.000	0.000	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.241, −0.273	0.265, −0.225	0.251, −0.268	0.387, −0.349	0.305, −0.301
Extinction method	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient	0.025 (5)	0.018 (6)	0.0039 (8)	0.033 (8)	0.035 (6)

Table 1 (continued)

	(6)	(7)
Crystal data		
Chemical formula	$C_{12}H_{13}N_2 \cdot C_{14}H_7N_4O_{12}$	$C_{12}H_{12}N_2 \cdot 2(C_7H_3N_2O_6)$
Chemical formula weight	608.48	606.46
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
a, b, c (Å)	10.1344 (6), 4.9420 (2), 27.5984 (14)	4.7297 (3), 9.3973 (6), 14.8365 (6)
α, β, γ (°)	90, 110.960 (2), 90	104.528 (3), 94.086 (3), 92.793 (3)
V (Å^3)	1290.78 (11)	635.20 (6)
Z	2	1
D_x (Mg m^{-3})	1.566	1.585
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	13 358	6274
θ range (°)	3.09–27.49	2.85–25.50
μ (mm^{-1})	0.127	0.129
Temperature (K)	150 (1)	150 (1)
Crystal form, colour	Block, colourless	Plate, colourless
Crystal size (mm)	0.32 × 0.25 × 0.20	0.16 × 0.12 × 0.06
Data collection		
Diffractometer	Kappa-CCD	Kappa-CCD
Data collection method	φ and ω scans with κ offsets	φ and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan
$T_{\min}$	0.9605	0.9797
$T_{\max}$	0.9751	0.9923
No. of measured, independent and observed parameters	13 358, 2838, 2287	6274, 2360, 1733
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.043	0.049
$\theta_{\max}$ (°)	27.49	25.50
Range of h, k, l	$0 \rightarrow h \rightarrow 13$ $-6 \rightarrow k \rightarrow 0$ $-35 \rightarrow l \rightarrow 32$	$0 \rightarrow h \rightarrow 5$ $-11 \rightarrow k \rightarrow 11$ $-17 \rightarrow l \rightarrow 17$
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0435, 0.1115, 1.045	0.0436, 0.109, 1.031
No. of reflections and parameters used in refinement	2838, 200	2360, 200
H-atom treatment	Constrained	Constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.4399P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.1435P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.239, −0.278	0.19, −0.255
Extinction method	None	*SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient	–	0.022 (4)

Computer programs used: *Kappa-CCD* server software (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *NRCVAX*96, *SHELXL*97 (Sheldrick, 1997*b*), *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 2000) *NRCVAX* (Gabe *et al.*, 1989) and *WordPerfect* macro PRPKAPPA (Ferguson, 1999).

the unit cell (Fig. 4) and the three component ions are linked by nearly linear N—H···O hydrogen bonds into a centrosymmetric aggregate. A single type of C—H···O hydrogen bond links these ionic aggregates into a molecular ladder. Atom C1 at (x, y, z) is a component of the cation centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and it acts as a donor, *via* H1*B*, to O1 in the anion at $(-1 + x, y, z)$, thus generating by translation a $C(7)$ chain running parallel to [100] (Fig. 8). The symmetry-related C1 in the same cation is at $(1 - x, 1 - y, 1 - z)$ and it acts as a donor to O1 in the anion at $(2 - x, 1 - y, 1 - z)$, thus generating another $C(7)$ chain, antiparallel to the first. Propagation of these interactions produces a molecular ladder in which the $C(7)$ chains form the uprights and the C—C bonds of the cations form the rungs. Between adjacent rungs there are $R_4^4(16)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer; Fig. 8). Two such ladders ran through each unit cell, but there are no close contacts between neighbouring ladders: the pendent aryl groups of adjacent ladders are loosely interleaved but there are no aromatic $\pi \cdots \pi$ stacking interactions.

The form of the one-dimensional array in (6) and (7) differs from that observed in (4) and is in each a chain of rings rather than a ladder. In both (6) and (7) (Figs. 6 and 7), the bipyridyl units lie across centres of inversion, chosen in each compound as $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The hard hydrogen bonds in (6) and (7) differ, as noted above (see §2.2) in that two half-occupied sites in (6) lead to a combination of N—H···O and O—H···N hydrogen bonds, while in (7) a single site leads to a centred N···H···O hydrogen bond. The net result in both compounds is, however, the formation of centrosymmetric three-component aggregates, analogous to that found in (4). Similarly, in each of (6) and (7) a single type of C—H···O hydrogen bond produces a chain of rings motif.

Table 2
Hydrogen-bond dimensions (Å, °).

D	H	A	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
(1)					
N1	H1*A*	O1^{i}	1.77	2.676 (2)	174
N1	H1*B*	O3	2.25	3.137 (2)	165
N1	H1	O2^{ii}	1.85	2.729 (2)	163
(2)					
N1	H1*A*	O1	1.80	2.695 (2)	165
N1	H1*B*	O2^{iii}	1.79	2.684 (2)	165
C2	H2*A*	O5^{iv}	2.45	3.191 (2)	131
(3)					
N1	H1	O12	1.32 (2)†	2.533 (2)	175.5 (5)
N2	H2	O22	1.70	2.629 (2)	175
C1	H1*B*	O14^{v}	2.46	3.342 (2)	148
C2	H2*B*	O11^{vi}	2.33	3.211 (2)	147
C6	H6*B*	O13^{vii}	2.49	3.306 (2)	139
C26	H26	O1^{viii}	2.26	3.180 (2)	162
(4)					
N2	H2	O2	1.72	2.648 (2)	173
C1	H1*B*	O1^{viii}	2.24	3.213 (2)	168
(5)					
N1	H1	O1	1.68	2.599 (2)	167
C2	H2*A*	O2^{ix}	2.45	3.238 (2)	137
C4	H4*A*	O2^{ix}	2.41	3.224 (2)	140
C4	H4*B*	O5^{x}	2.46	3.339 (2)	149
(6)					
N1	H1*A*	O1	1.65	2.521 (2)	170
O1	H1	N1	1.70	2.521 (2)	167
C5	H5	O2^{xi}	2.39	3.241 (2)	148
(7)					
N11	H11	O1	1.33‡	2.509 (2)	164
C12	H12	O5^{xii}	2.46	3.362 (2)	158

Symmetry codes: (i) $-1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, 1-y, 1-z$; (iv) $x, y, -1+z$; (v) $1-x, 1-y, -z$; (vi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (viii) $-1+x, y, z$; (ix) $2-x, 1-y, 1-z$; (x) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (xi) $2-x, 2-y, 1-z$; (xii) $-1-x, 2-y, 2-z$. † N1—H1 1.21 (2) Å. ‡ N11—H11 1.20 Å.

In (6) atom C5 at (x, y, z), which is a component of the bipyridyl centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a donor to carboxylate O2 in the anion at $(2-x, 2-y, 1-z)$: this anion is part of the three-component aggregate centred at $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$. The symmetry-related C5 in the same diamine centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is at $(1-x, 1-y, 1-z)$ and this atom acts as a donor to O2 at $(-1+x, -1+y, z)$, which is part of the three-component aggregate centred at $(0, 0, \frac{1}{2})$. In this manner, a $C_2^2(13)$ $[R_4^4(16)]$ chain of rings is generated running parallel to the [110] direction (Fig. 9), with the bipyridyl units centred at $(n+\frac{1}{2}, n+\frac{1}{2}, \frac{1}{2})$ and the $R_4^4(16)$ rings centred at $(n, n, \frac{1}{2})$ (n = zero or integer). This chain of rings lies in the domain $0.22 < z < 0.78$: a second such chain, generated from the first by the action of the glide plane and running parallel to the $[1\bar{1}0]$ direction, lies in the domain $0.72 < z < 1.28$. There are neither soft hydrogen bonds, nor aromatic $\pi\cdots\pi$ stacking interactions between neighbouring chains.

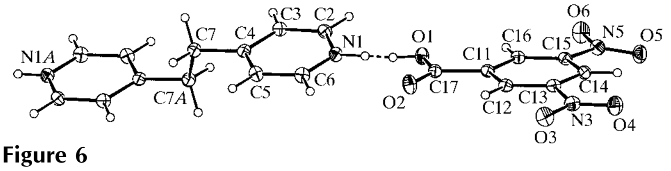

Figure 6
The molecular components of (6), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked *A* are at the symmetry position $(1-x, 1-y, 1-z)$. The H atom between O1 and N1 is disordered (see text).

The soft hydrogen bond in (7) differs from that in (6) in that in (7) it is a nitro group O atom which acts as the acceptor, whereas in (6) the acceptor is a carboxylate O, which accepts the C—H$\cdots$O hydrogen bond. In (7) atom C12 at (x, y, z) acts as a donor to O5 at $(-1-x, 2-y, 2-z)$: propagation of the N—H$\cdots$O and C—H$\cdots$O hydrogen bonds by translation and inversion leads to a $C_2^2(18)$ $[R_4^4(22)]$ chain of rings running parallel to the $[\bar{2}11]$ direction (Fig. 10). The space group for (7) is $P\bar{1}$, so that just one chain of rings is sufficient to define the entire crystal structure: as in (6) there are no significant bonding interactions between adjacent chains

Soft hydrogen bonds generate two-dimensional arrays: In contrast to the foregoing compounds, the cations in (3) lie in general positions. Reflecting the idealized D_{3h} molecular

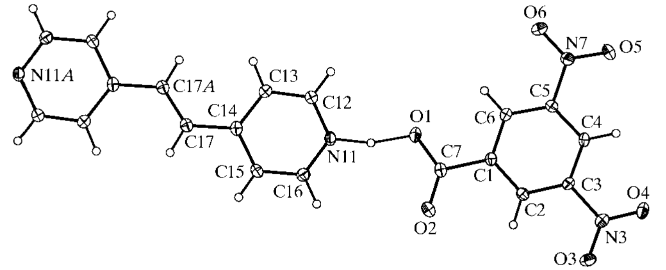

Figure 7
The molecular components of (7), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms marked *A* are at the symmetry position $(1-x, 1-y, 1-z)$.

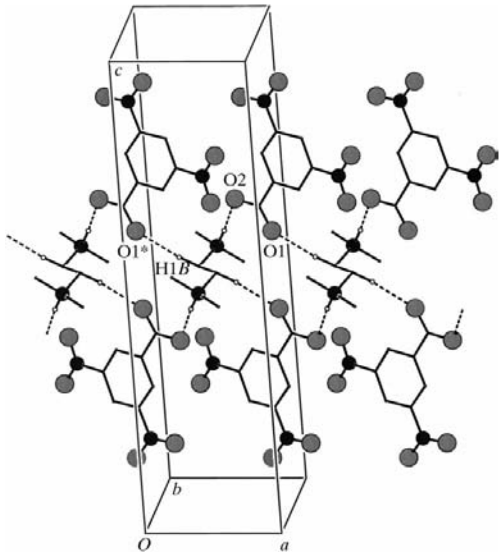

Figure 8
Part of the crystal structure of (4), showing the formation of a molecular ladder parallel to [100]. H atoms not involved in the hydrogen bonding motif shown are omitted for the sake of clarity. The atom marked with a star (*) is at the symmetry position $(-1+x, y, z)$.

symmetry of the diamine 1,4-diazabicyclo[2.2.2]octane, examples are known where this diamine lies across a twofold rotation axis (Ferguson *et al.*, 1997) or on a mirror plane (Meehan *et al.*, 1997): more surprisingly, it has also been observed to lie disordered across a centre of inversion (Ferguson *et al.*, 1998). As previously noted (see §2.2) the two hard hydrogen bonds within the asymmetric unit (Fig. 3) differ in the location of their H atoms. Similarly, the behaviour of the two independent anions is different in that only one of them is an acceptor of C—H···O hydrogen bonds, utilizing both carboxylate and nitro group O atoms as acceptors (Table 2). The other anion does not participate at all in the formation of soft hydrogen bonds between the ions.

The two-dimensional array generated by the soft hydrogen bonds is most readily analysed and described in terms of distinct one-dimensional motifs, each generated by a different C—H···O hydrogen bond. There is a spiral chain running parallel to the [010] direction and a zigzag chain running parallel to [001]. In the first, atom C2 at (x, y, z) acts as a donor, *via* H2*B*, to O11 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, while C2 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ likewise acts as a donor to O11 at $(x, 1+y, z)$, thus producing a $C_2^2(7)$ spiral generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{2})$ (Fig. 11). In the second chain motif, C6 in the same cation at (x, y, z) acts as a donor, *via* H6*B*, to nitro O13 at $(x, \frac{3}{2}-y, \frac{1}{2}+z)$, and propagation of this interaction in concert with the N1—H1···O12 hydrogen bond produces a $C_2^2(12)$ chain generated by the glide plane at $y = \frac{3}{4}$ (Fig. 12). The combination of the [010] and [001] chains generates a sheet parallel to (100) which incorporates all the ionic components within the unit cell.

As well as the C—H···O hydrogen bonds involved in the formation of the [010] and [001] chains, there is a third type of C—H···O hydrogen bond lying within the (100) sheet. Atom C1 at (x, y, z) acts as a donor, *via* H1*B*, to O14 in the anion at $(1-x, 1-y, -z)$ thus producing a centrosymmetric $R_4^4(22)$ motif (Fig. 13).

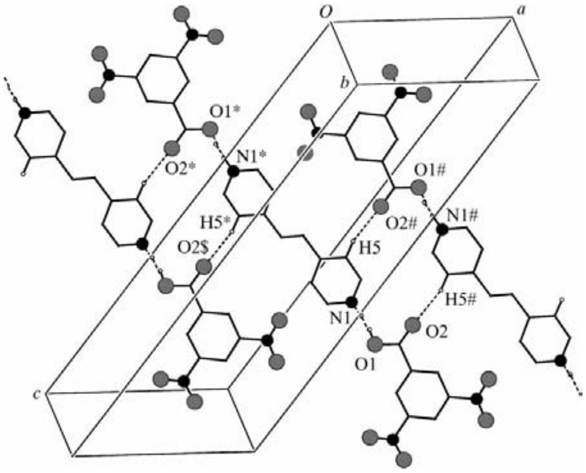

Figure 9
Part of the crystal structure of (6), showing the formation of a $C_2^2(13)$ $[R_4^4(16)]$ chain of rings parallel to [110]. Atoms are depicted as in Fig. 8. The atoms marked with a star (*), hash (#) or dollar sign ($) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(2-x, 2-y, 1-z)$ and $(-1+x, -1+y, z)$, respectively.

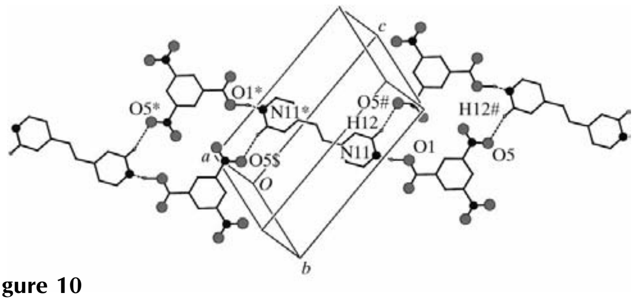

Figure 10
Part of the crystal structure of (7), showing the formation of a $C_2^2(18)$ $[R_4^4(22)]$ chain of rings parallel to $[\bar{2}11]$. Atoms are depicted as in Fig. 8. The atoms marked with a star (*), hash (#) or dollar sign ($) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(-1-x, 2-y, 2-z)$ and $(2+x, -1+y, -1+z)$, respectively.

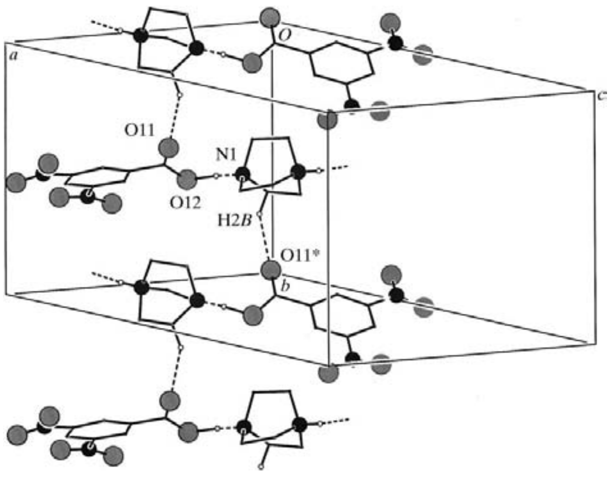

Figure 11
Part of the crystal structure of (3), showing the formation of a $C_2^2(7)$ spiral parallel to [010]. Atoms are depicted as in Fig. 8. The atom marked with a star (*) is at the symmetry position $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

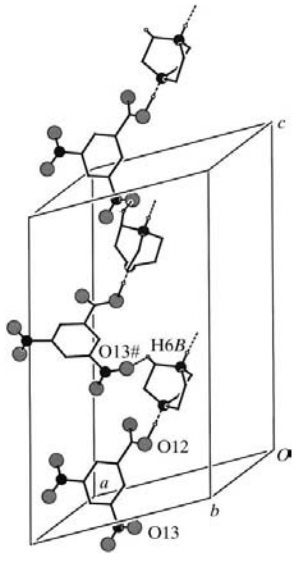

Figure 12
Part of the crystal structure of (3), showing the formation of a $C_2^2(12)$ zigzag chain parallel to [001]. Atoms are depicted as in Fig. 8. The atom marked with a hash (#) is at the symmetry position $(x, \frac{3}{2}-y, \frac{1}{2}+z)$.

In addition to the ions, there is also a low-occupancy water component in the structure, with site occupation factor 0.130 (5). Although the H atoms associated with the water O1 could not be located, the O$\cdots$O distances around O1 are clearly indicative of hydrogen bonding: thus O1$\cdots$O11 2.733 (2), O1$\cdots$O21$^{\rm i}$ [(i) = $1+x, y, z$] 2.838 (2) and O1$\cdots$O24$^{\rm ii}$ [(ii) = $1+x, \frac{1}{2}-y, -\frac{1}{2}+z$] 2.756 (2) Å (Fig. 14). None of these O atoms carries any H and clearly a neutral water molecule with ordered H atoms cannot act as a threefold donor of hydrogen bonds: one interpretation is that there is disorder, probably dynamic with two H atoms mobile between three sites (Aliev *et al.*, 1998; Serrano-González *et al.*, 1999). Additionally O1 acts as an acceptor in a C—H$\cdots$O hydrogen bond (Table 2). The multiple hydrogen-bonded neighbours of O1 suggest that its presence is not fortuitous: the surprise perhaps is that this site is not fully occupied. Full occupancy of this site would, in fact, lead to the generation of a three-dimensional framework as O1 would then serve to link neighbouring (100) sheets.

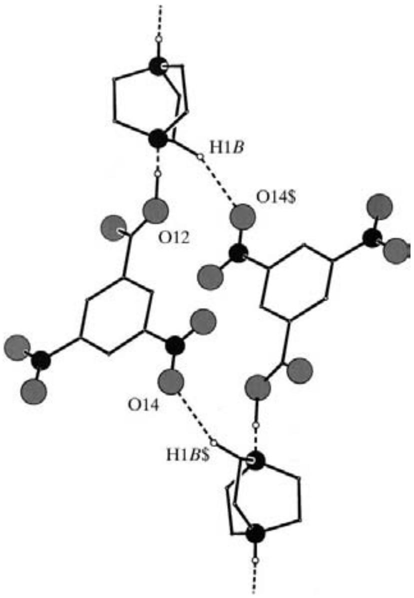

Figure 13
Part of the crystal structure of (3), showing the formation of a centrosymmetric $R^4_4(22)$ ring within a (100) sheet. Atoms are depicted as in Fig. 8. The atoms marked with a dollar sign ($) are at the symmetry position $(1-x, 1-y, -z)$.

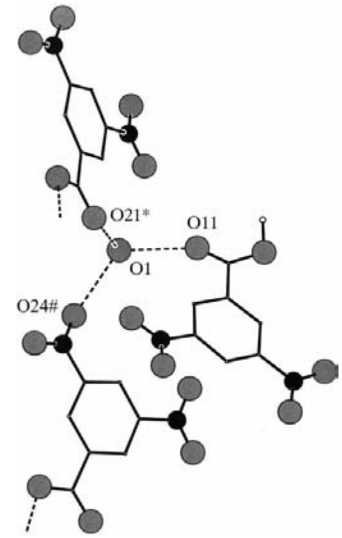

Figure 14
Part of the crystal structure of (3), showing the short O$\cdots$O contacts around the water atom O1. H atoms bonded to C are omitted for the sake of clarity. The atoms marked with a star (*) or a hash (#) are at the symmetry positions $(1+x, y, z)$ and $(1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, respectively.

Soft hydrogen bonds generate three-dimensional arrays: In (5) (Fig. 5) the supramolecular aggregation is dominated by the occurrence of three distinct C—H$\cdots$O hydrogen bonds involving both carboxylate and nitro O atoms as acceptors. The cation in (5) lies across a centre of inversion, once again chosen as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the single N—H$\cdots$O hydrogen bond between cation and anion once again generates a centrosymmetric three-component aggregate. (Fig. 15). These units are linked into a chain of multiply fused rings by two types of C—H$\cdots$O hydrogen bonds. Atoms C2 and C4 are both adjacent to the charged N centre and these atoms at (x, y, z) both act as donors, *via* H2*A* and H4*A*, respectively, to the same acceptor, O2 in the anion at $(2-x, 1-y, 1-z)$, which is part of the three-component aggregate centred at $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$. These paired C—H$\cdots$O interactions generate an $R^1_2(6)$ ring with a chair conformation. Two such rings are generated by each cation, thus producing a sequence of three *trans*-fused chair-type rings: pairs of $R^1_2(6)$ rings, related by the centres of inversion at $(n, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer) themselves enclose $R^4_4(14)$ rings (Fig. 15).

The formation of this chain of rings utilizes the N—H$\cdots$O hydrogen bond and two of the C—H$\cdots$O hydrogen bonds: by the use of just the N—H$\cdots$O hydrogen bonds and the final C—H$\cdots$O hydrogen bond, a continuous sheet is generated parallel to (100) in the form of a (4, 4) net. Atom C4 at (x, y, z) acts as a donor, *via* H4*B*, to nitro O5 at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, while

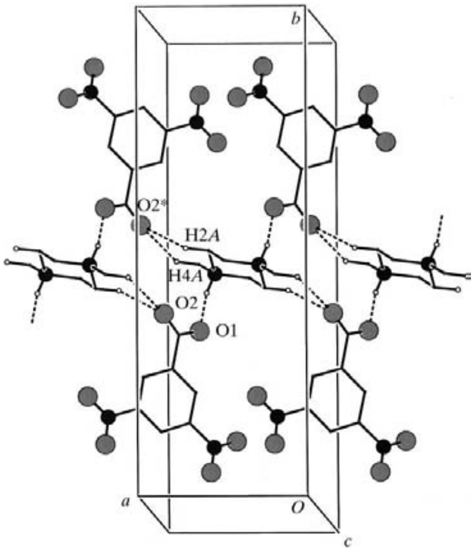

Figure 15
Part of the crystal structure of (5), showing the formation of a chain of fused rings parallel to [100]. Atoms are depicted as in Fig. 8. The atom marked with a star (*) is at the symmetry position $(2-x, 1-y, 1-z)$.

C4 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ in turn acts as a donor to O5 at $(x, y, 1 + z)$. The combination of this C(11) zigzag chain with the centres of inversion at each cation generates a continuous sheet built from a single type of $R^8_8(50)$ ring (Fig. 16). The combination of these (100) sheets with the [100] chains (Fig. 15) serves to link all the components into a single three-dimensional framework.

3.2.2. Hard hydrogen bonds generate continuous chains. In (2) (Fig. 2), the hard N—H$\cdots$O hydrogen bonds generate a one-dimensional array in the form of a chain of rings, and the soft C—H$\cdots$O hydrogen bonds link these chain into sheets, so that the overall supramolecular aggregation is two-dimensional.

Each cation acts as a donor of N—H$\cdots$O hydrogen bonds to four different anions and each anion acts as an acceptor of such bonds from two different cations. With the reference $[H_2N(CH_2CH_2)_2NH_2]^{2+}$ cation placed at the centre of the unit cell, across a centre of inversion, N1 at (x, y, z) acts as a donor *via* H1*A* and H1*B*, respectively, to carboxylate atoms O1 at (x, y, z) and O2 at $(-x, 1 - y, 1 - z)$, respectively. The symmetry-related N1 at $(1 - x, 1 - y, 1 - z)$ in the same cation similarly acts as a donor to O1 at $(1 - x, 1 - y, 1 - z)$ and to O2 at $(1 - x, y, z)$. Propagation of these interactions generates a $C^2_2(9)$ $[R^4_4(12)]$ chain of rings running parallel to [100] (Fig. 17). The cations are centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the $[R^4_4(12)]$ rings are centred at $(n, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer): a single chain of this type runs through each unit cell and suffices to define the structure.

A single type of C—H$\cdots$O hydrogen bond then links these [100] chains into sheets. Atom C2 at (x, y, z), a component of the cation, acts as a donor, *via* H2*A*, to nitro group O5 at $(x, y, -1 + z)$ and propagation of this interaction by inversion and translation produces a second chain of rings, of $C^2_2(11)$ $[R^4_4(24)]$ type, running parallel to [001] (Fig. 18), in which the $R^4_4(24)$ rings are centred at $(\frac{1}{2}, \frac{1}{2}, n)$ (n = zero or integer).

The combination of these two types of chains of rings, along [100] and [001] generates continuous sheets parallel to (010). Despite the fact that all the aryl rings in the structure are in parallel planes, there are no aromatic $\pi\cdots\pi$ stacking interactions between adjacent rings: there are no centroid$\cdots$centroid distances below 4.80 Å.

3.2.3. Hard hydrogen bonds generate a three-dimensional framework. There have been two previous reports on the structure of the salt (1) formed by 3,5-dinitrobenzoic acid and 1,2-diaminoethane. For the triclinic phase (Nethaji *et al.*, 1992) no H atom positions were reported: the monoclinic phase has been studied at 295 K (Lynch *et al.*, 1994). The present study at 150 K clearly relates to the same monoclinic phase as that studied earlier, but the determination reported here is more precise. Moreover, the discussion of the supramolecular aggregation given by Lynch *et al.* (1994) was very brief and seriously incomplete: consequently, we discuss here a full analysis of this aggregation.

The cation $[H_3NCH_2CH_2NH_3]^{2+}$ (Fig. 1) again lies across a centre of inversion, chosen for convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and it acts as a sixfold donor in N—H$\cdots$O hydrogen bonds. The anion, which lies in a general position, is a threefold acceptor of N—H$\cdots$O hydrogen bonds, with both of the carboxylate O atoms and one of the nitro group O atoms acting as the acceptors: by contrast with all of the other compounds discussed in this paper, there are no C—H$\cdots$O hydrogen bonds in the crystal structure of (1).

Four of the N—H bonds in each cation act as donors to carboxylate O atoms (Table 2) and so generate a $C^2_2(9)$ $[R^4_4(12)]$ chain of rings running parallel to [100] (Fig. 19), entirely analogous to that formed in the piperazinium salt (2) (see §3.2.2). These chains run along (*x*, 0, 0) and along the cell edges (*x*, 0, 0), (*x*, 0, 1) and so on. The formation of such a chain utilizes only four of the six N—H bonds in the cation and the remaining two such bonds form N—H$\cdots$O hydrogen bonds which link the [100] chains into a continuous framework. Atom N1 at (x, y, z), which is a component of the [100] running along $(x, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor, *via* H1*B*, to O3 also at (x, y, z): O1 in the same anion at (x, y, z) is

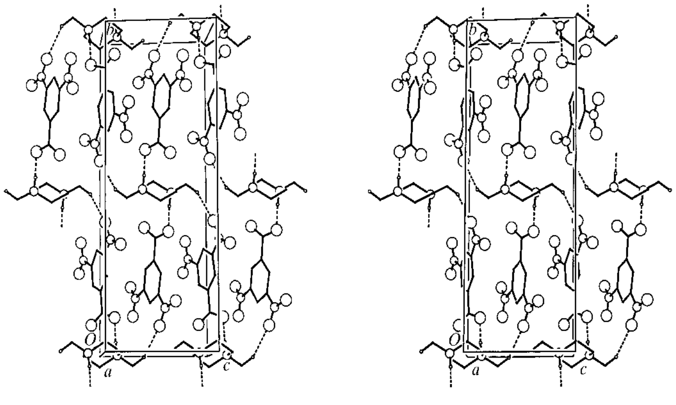

Figure 16
Stereoview of part of the crystal structure of (5), showing the formation of a (100) sheet built from $R^8_8(50)$ rings. Atoms are depicted as in Fig. 8.

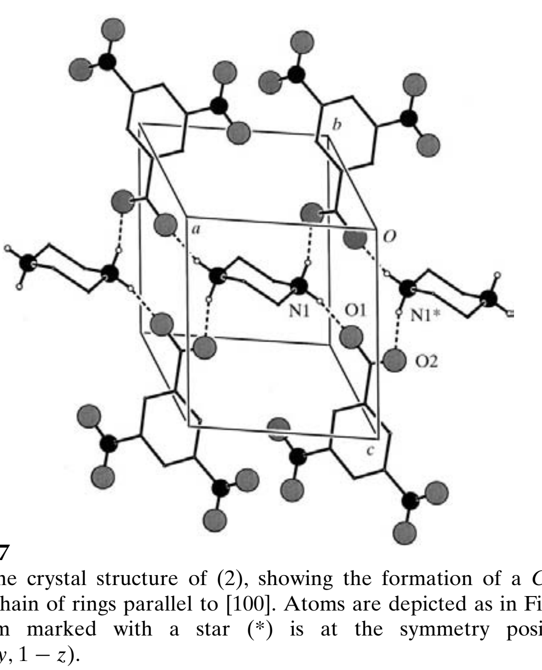

Figure 17
Part of the crystal structure of (2), showing the formation of a $C^2_2(9)$ $[R^4_4(12)]$ chain of rings parallel to [100]. Atoms are depicted as in Fig. 8. The atom marked with a star (*) is at the symmetry position $(-x, 1 - y, 1 - z)$.

an acceptor from N1 at $(1+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, which is a component of the [100] chain along $(x, 0, 0)$. In this manner a $C_2^2(10)$ motif is produced running parallel to $[20\bar{1}]$ (Fig. 20) and generated by the glide plane at $y = \frac{1}{4}$. Propagation of this $C_2^2(10)$ motif by the space group serves to link each of the [100] chains to its four nearest-neighbour chains, thus producing a single, continuous three-dimensional framework.

In the original report on this structure (Lynch *et al.*, 1994) only the $R_4^4(12)$ ring motif was identified. The formation of the [100] chains of rings and the linking of these chains into a framework were not discussed at all: indeed the structural consequences of the hydrogen bond to the nitro group was not considered. Hence, the original supramolecular description is very far from complete. Although no H atom positions were reported for the triclinic phase (Nethaji *et al.*, 1992), the 1,2-diaminoethane component lies across a centre of inversion at $(\frac{1}{2}, 0, \frac{1}{2})$ and the N$\cdots$O distances: N$\cdots$O(carboxylate)$^{\rm i}$ 2.666 (3), N$\cdots$O(carboxylate)$^{\rm ii}$ 2.700 (3), N$\cdots$O(nitro)$^{\rm iii}$ 3.085 (3) Å [symmetry codes: (i) $x, -1+y, z$; (ii) $1-x, -y, 1-z$; (iii) $1+x, y, 1+z$] are extremely similar to those found here for (1) (Table 2); assuming that these short contacts represent hard hydrogen bonds, they define a supramolecular structure of exactly the same type as discussed above.

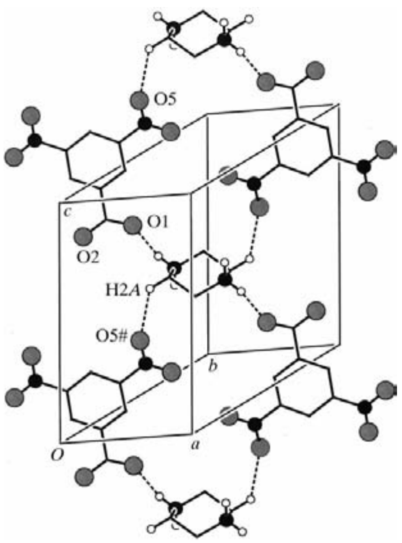

Figure 18
Part of the crystal structure of (2), showing the formation of a $C_2^2(11)$ $[R_4^4(24)]$ chain of rings parallel to [001]. Atoms are depicted as in Fig. 8. The atom marked with a hash (#) is at the symmetry position $(x, y, -1+z)$.

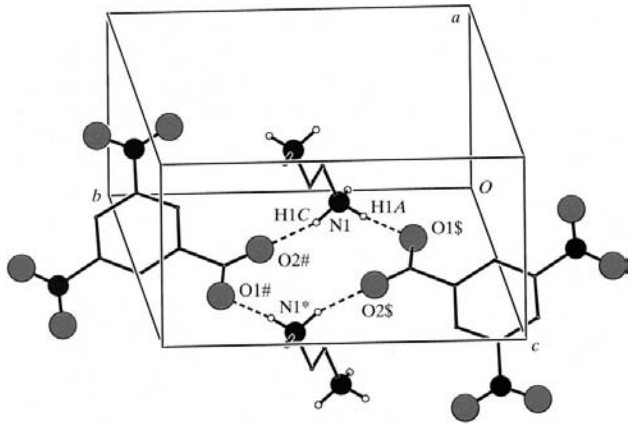

Figure 19
Part of the crystal structure of (1), showing the formation of a $C_2^2(9)$ $[R_4^4(12)]$ chain of rings parallel to [100]. Atoms are depicted as in Fig. 8. The atoms marked with a star (*), hash (#) or dollar sign ($) are at the symmetry positions $(-x, 1-y, 1-z)$, $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ and $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, respectively.

3.3. Hydrogen-bond dimensions

The hard hydrogen bonds (Table 2) are nearly all of N—H$\cdots$O type: the sole exception occurs in (6) where an H atom is disordered over two sites along the N$\cdots$O vector, one closer to N and the other closer to O. The majority of the N—H$\cdots$O hydrogen bonds involve a carboxylate O as the acceptor and here the sole exception occurs in (1) where one of these bonds utilizes a nitro group O atom as an acceptor. Since all those using carboxylate acceptors are charge-assisted hydrogen bonds of the type N$^+$—H$\cdots$O$^-$, they are short; for those hydrogen bonds in which the H atoms are fully ordered, the H$\cdots$O distances range from 1.65 Å in (6) to 1.85 Å in (1), while the N$\cdots$O distances, regardless of H atom ordering, lie in the range 2.509 (2) Å in (7) to 2.729 (2) Å in (1). Those with N$\cdots$O distances less than 2.60 Å can be regarded as strong hydrogen bonds (Steiner *et al.*, 2000). Associated with these short H$\cdots$O and N$\cdots$O distances are N—H$\cdots$O angles ranging from 163° in (1) to 175.5 (5)° in (3), with a mean value of 169°. By contrast, the sole N—H$\cdots$O hydrogen bond utilizing a nitro group O atom as an acceptor in (1) has significantly longer H$\cdots$O and N$\cdots$O distances and is correspondingly weaker, even though the acceptor atom carries a substantial net negative charge. Since the N—H$\cdots$O frag-

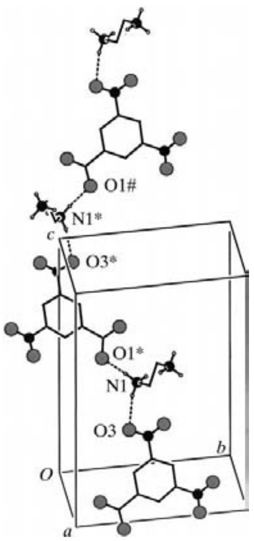

Figure 20
Part of the crystal structure of (1), showing the formation of one of the $C_2^2(10)$ chains along $[20\bar{1}]$, which link the [100] chains. Atoms are depicted as in Fig. 8. The atoms marked with a star (*) or hash (#) are at the symmetry positions $(-1+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(-2+x, y, 1+z)$, respectively.

ments are all close to linearity, there is a fairly close correlation between the variation of the H···O distances and that of the N···O distances.

The soft C—H···O hydrogen bonds are of two types, involving aromatic and aliphatic C—H bonds, respectively. The ranges of the C···O distances for the two types of interaction are almost identical (Table 2), although the H···O distances range between 2.24 and 2.45 Å (mean 2.26 Å) for anionic acceptors, and between 2.45 and 2.49 Å (mean 2.46 Å) for neutral acceptors. The C—H···O angles are noticeably larger for those bonds utilizing aromatic donors. All are short for their type. The extensive involvement of aliphatic C—H bonds is noteworthy, but in every case the C—H bond is adjacent to a cationic N atom: this increases the acidity of the neighbouring C—H bonds, thus enhancing their capability for C—H···O hydrogen-bond formation.

3.4. Molecular conformations and dimensions

The cations in (1) and (4) are both centrosymmetric and thus the central N—C—C—N core in each has a fully staggered *trans*-planar conformation. Full staggering is not maintained throughout the cation of (4), as the two independent C—N—C—C torsional angles involving the terminal methyl groups are 73.6 (2) and −163.0 (2)°: perfect staggering requires angles of 60 and 180°, respectively. The rotation of the HMe_2N groups relative to the N—C—C—N core may be associated with the formation of the short and strong N—H···O hydrogen bonds (Table 2). In (2) and (5) the cations are again centrosymmetric: both cations thus adopt chair conformations and in (5) the *N*-methyl groups are in equatorial sites, as expected.

Centrosymmetric cations also occur in (6) and (7), so that the central aliphatic fragments, C—C—C—C and C—C=C—C, respectively, are both *trans*-planar. The only conformational degree of freedom in these cations arises from the twist of the pyridyl rings relative to the C_4 cores. In (7) the cation is almost planar, with a pyridyl twist angle of only 7.2 (2)°, while in (6) the corresponding angle is 68.6 (2)°. While it is tempting to ascribe this conformational difference to extended π-conjugation in (7), the bond lengths provide no support for this. There is no evidence in (7) of the type of orientation disorder observed in the analogous adduct formed by this diamine with 4,4-sulfonyldiphenol (Ferguson, Glidewell, Gregson & Meehan, 1999).

The cation of (3) is the only one in this series which lies in a general position. As usual, the heavy-atom framework is twisted away from the optimum $D_{3h}(\bar{6}m2)$ symmetry, which requires fully eclipsed CH_2 groups to a conformation of D_3 (32) symmetry: however, the magnitude of this distortion, as indicated by the N—C—C—N torsional angles, mean value −13.7°, is somewhat greater than those usually observed (Glidewell *et al.*, 1999).

In the anions, the carboxylate groups and the nitro groups all exhibit modest rotations away from the planes of the adjacent aryl rings: for the carboxylate group these rotations range from 1.2 (2)° in (3) to 24.1 (2)° in (5); for the nitro groups the corresponding range is 0.2 (2)° in (6) to −13.4 (2)° in (5). For neither substituent is there any obvious pattern to its conformational behaviour: in particular, there is no indication of any systematic influence of the hydrogen bonding on the anion conformations.

The bond lengths and angles show no unusual features.

3.5. Structures of related compounds

Two other adducts formed between 3,5-dinitrobenzoic acid and aromatic diamines were retrieved from the Cambridge Structural Database (CSD: Allen & Kennard, 1993). For the 2:1 adduct formed with 1,10-phenanthroline (KUFCET; Byriel *et al.*, 1992), no coordinates are recorded in the CSD and from the original paper it appears that although the adduct has been prepared its structure has not actually been determined. Since this diamine can act as both a chain-builder and a chain-terminator (Ferguson, Glidewell & Lavender, 1999), this adduct is certainly worthy of further study. The adduct formed with phenazine (ZUPKUQ; Pedireddi *et al.*, 1996) has 1:1 stoichiometry, rather than the usual 2:1 stoichiometry. The structure contains only neutral molecules and consists of finite centrosymmetric aggregates, in which pairs of diamines are linked by paired C—H···N hydrogen bonds in an $R_2^2(8)$ motif, while two acid molecules are linked to this diamine dimer by a combination of strong O—H···O and weak C—H···O hydrogen bonds. The adduct ZUPKUQ is thus radically different from all those described in this paper.

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC (Canada).

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