research communications

Different cation-protonation patterns in molecular salts of unsymmetrical dimethyhydrazine: $C_2H_9N_2 \cdot Br$ and $C_2H_9N_2 \cdot H_2PO_3$

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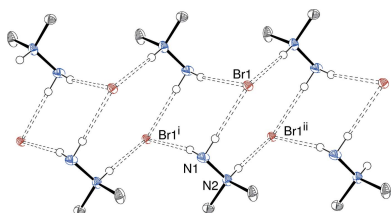
We describe the syntheses and crystal structures of two molecular salts containing the 1,1-dimethylhydrazinium cation, namely 1,1-dimethylhydrazin-1-ium bromide, $C_2H_9N_2^+ \cdot Br^-$, (I), and 2,2-dimethylhydrazin-1-ium dihydrogen phosphite, $C_2H_9N_2^+ \cdot H_2PO_3^-$, (II). In (I), the cation is protonated at the methylated N atom and $N-H \cdots Br$ hydrogen bonds generate [010] chains in the crystal. In (II), the cation is protonated at the terminal N atom and cation-to-anion $N-H \cdots O$ and anion-to-anion $O-H \cdots O$ hydrogen bonds generate (001) sheets.

1. Chemical context

Unsymmetrical dimethylhydrazine (1,1-dimethylhydrazine; $C_2H_8N_2$; UDMH) is a colourless liquid at room temperature and pressure with a strong and unpleasant ammonia-like or fishy smell. The best known application of this compound is the fuel (reducing agent) in hypergolic rocket fuels (Edwards, 2003), where it can be used alone or mixed with hydrazine: the latter formulation (trade name 'Aerozine 50') was used by the Apollo lunar modules to begin their homeward journeys from the moon.
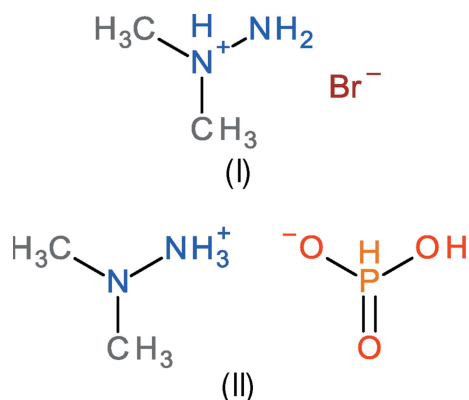
Chemically, both nitrogen atoms in UDMH bear lone pairs of electrons, which can act as weak bases to accept protons and therefore result in the formation of molecular salts when reacted with acids. The first crystal structure of a UDMH salt was reported by Klapötke *et al.* (1999), who prepared 1,1-dimetylhydrazinium azide as a possible high-energy-density material with military applications; the methylated UDMH nitrogen atom is protonated and the components are linked by strong $N-H \cdots N$ hydrogen bonds in the crystal. However, this salt exhibited pronounced hygroscopic behaviour and had a low melting point of 311 K, which deemed it unsuitable for such uses. The nitrate salt of UDMH, which may be a decomposition product of hypergolic fuels, was prepared soon afterwards by the same workers (De Bonn *et al.*, 2001) by a low-temperature, non-aqueous synthesis: anhydrous nitric acid and UDMH were separately dissolved in dichloromethane at 195 K and the solutions mixed at the same temperature. The resulting hygroscopic salt, 1,1-dimethylhydrazinium nitrate, is protonated at the methylated nitrogen atom and features $N-H \cdots O$ hydrogen bonds in its crystal structure.

Merkoulov *et al.* (2005) synthesized 1,1-dimethylhydrazinium chloride by reacting liquid UDMH with HCl dissolved in diethyl ether: its crystal structure consists of two

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independent cations and two chloride anions in the asymmetric unit. The cation is protonated at the methylated nitrogen atom and a dense network of strong N—H⋯Cl and weak C—H⋯Cl hydrogen bonds helps to consolidate the packing in the crystal. A salt with a more complicated counterion was synthesised by Mu *et al.* (2011): the addition of liquid UDMH to a solution of picric acid in ethanol at room temperature yielded 1,1-dimethylhydrazinium picrate. As before, the UDMH protonates at the methylated nitrogen atom and cation-to-anion N—H⋯O hydrogen bonds help to establish the packing.

(I)

(II)

As an extension of these studies, we now describe the syntheses and crystal structures of 1,1-dimethylhydrazin-1-ium bromide, $C_2H_9N_2^+ \cdot Br^-$ (I) and 2,2-dimethylhydrazin-1-ium dihydrogen phosphite, $C_2H_9N_2^+ \cdot H_2PO_3^-$ (II).

2. Structural commentary

Compound (I) crystallizes in space group $I2/a$ (non-standard setting of $C2/c$) with one cation and one bromide anion in the asymmetric unit (Fig. 1). The cation is protonated at the central N2 atom, as seen in previous UDMH salts referred to above. The N1—N2 bond length [1.4478 (19) Å] is slightly shorter than the C—N bond lengths [1.482 (2) and 1.485 (2) Å]. N2 is displaced from N1, C1 and C2 by 0.4834 (16) Å and the C—N—C bond angle [111.38 (14)°] is
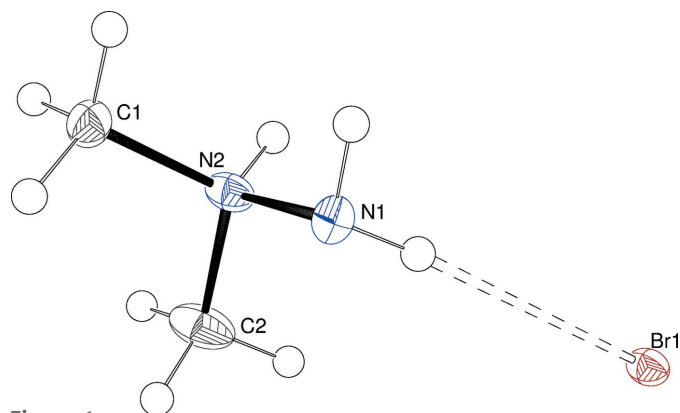

Figure 1
The molecular structure of (I), showing 50% displacement ellipsoids. The N—H⋯Br hydrogen bond is indicated by a double-dashed line (Table 1).

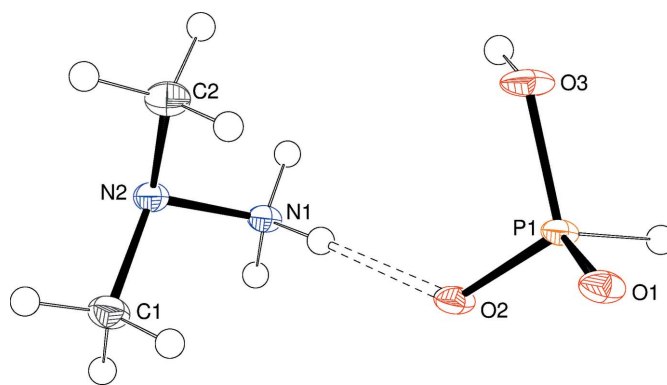**Figure 2**
The molecular structure of (II), showing 50% displacement ellipsoids. The N—H⋯O hydrogen bond is indicated by a double-dashed line (Table 2).

slightly greater than the C—N—N angles [108.93 (12) and 108.97 (14)°]. The H atoms attached to N1 point away from the carbon atoms [C1—N2—N1—H2n = −175.7 (2); C2—N2—N1—H1n = 178.0 (2)°] and the N2—H3n bond bisects the N1H$_2$ group [H3n—N2—N1—H1n = 61 (2)°].

Compound (II) crystallizes in space group $Pna2_1$ with one cation and one dihydrogen phosphite anion in the asymmetric unit (Fig. 2). In this case, the cation is protonated at the terminal N atom rather than the central N atom, which has not been seen previously in UDMH salts. The N1—N2 bond length is 1.454 (3) Å and the C—N bond lengths are 1.462 (3) and 1.463 (3) Å. The geometry about N2 is pyramidal and this atom is displaced from N1, C1 and C2 by 0.504 (2) Å. The bond angles about N2 show the same trend as those in (I): C—N—C = 110.69 (18); C—N—N = 107.62 (17) and 107.94 (18)°. Two of the H atoms attached to N1 have almost the same locations as the corresponding atoms in (I), whereas the third bisects the C1—N2—C2 grouping [C1—N2—N1—H3n = −62°]. In the anion, the P1—O3 bond length of 1.5638 (16) Å is typical (Harrison, 2003) for the protonated O atom in a dihydrogen phosphite group whereas P1—O1 [1.4982 (15) Å] and P1—O2 [1.5003 (16) Å] are almost the same length, indicating the expected delocalization (resonance) of the negative charge over these two O atoms. The O—P—O bond angle for the unprotonated oxygen atoms [116.76 (9)°] is significantly larger than the O—P—OH angles [106.37 (9) and 111.46 (9)°], as seen previously for similar species (Harrison, 2003). P1 is displaced from its attached O atoms by 0.4510 (13) Å.

3. Supramolecular features

In the crystal of (I), N—H⋯Br hydrogen bonds (Table 1) link the components into [010] chains (Fig. 3): each Br$^-$ ion accepts three N—H⋯Br bonds and alternating, centrosymmetric $R_4^2(8)$ and $R_4^2(10)$ loops occur within the chain. The N2 bond is significantly shorter than the N1 bonds, which may be due to the positive charge residing on N2: this was also observed in the structure of the nitrate salt (de Bonn *et al.*, 2001). There

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H1n···Br1^i	0.89 (2)	2.68 (3)	3.5666 (15)	170.7 (18)
N1—H2n···Br1	0.89 (2)	2.62 (2)	3.5117 (14)	175.0 (19)
N2—H3n···Br1^{ii}	0.87 (2)	2.39 (2)	3.2490 (13)	173.3 (17)
C1—H1a···Br1^i	0.98	3.11	3.9690 (18)	148
C1—H1b···Br1^{iii}	0.98	3.09	4.0175 (19)	158
C1—H1c···Br1^{iv}	0.98	2.90	3.8682 (17)	168
C2—H2c···Br1^{iii}	0.98	3.07	3.9843 (18)	156

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H1n···O1^i	0.91	1.83	2.736 (2)	176
N1—H2n···O1^{ii}	0.91	1.85	2.762 (2)	176
N1—H3n···O2	0.91	1.91	2.814 (2)	175
O3—H1o···O2^i	0.87	1.74	2.568 (2)	159

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

are also several weak C—H···Br contacts (Table 1) in (I); the weak and strong interactions result in each bromide ion accepting a total of seven hydrogen bonds (Fig. 4).

The crystal structure of (II) appears to correlate with the novel protonation pattern of the $C_2H_9N_2{}^+$ cation: the three H atoms attached to N1 each partake in a strong, near-linear N—H···O hydrogen bond to nearby $H_2PO_3{}^-$ anions (Table 2). The anions are linked into [100] chains by O—H···O hydrogen bonds with adjacent anions in the chain related by a-glide symmetry. Together, these interactions generate (001) sheets (Fig. 5) As usual (Harrison, 2001), the P—H grouping of the anion does not participate in hydrogen bonds and the H atom points into the inter-layer region.

4. Database survey

A search of the Cambridge Structural Database (CSD; Groom *et al.*, 2016) revealed the crystal structures of the four UDMH

Figure 4
The environment of the bromide ion in the crystal of (I). [Symmetry codes: (i) $\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-y$; (iv) $x, \frac{3}{2}-y, z-\frac{1}{2}$.] Note that each of the five cations has a different bonding mode: η^1 N1, N2 and C1 and η^2 N1 + C1 and C1 + C2.

derivatives cited above: refcodes for the azide, nitrate, chloride and picrate salts are CORRUW, IBOLOA, FOHLUK and AZUXID, respectively.

5. Synthesis and crystallization

Caution! UDMH is toxic, potentially carcinogenic and may form explosive mixtures with oxidizing agents: all appropriate
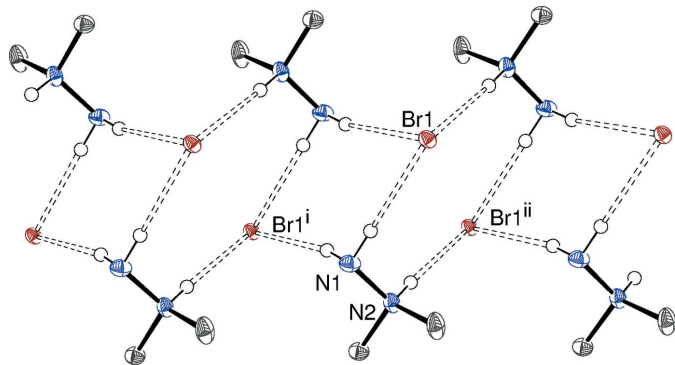

Figure 3
Partial packing diagram for (I), showing the formation of [010] chains linked by N—H···Br hydrogen bonds. C-bound H atoms are omitted for clarity. Symmetry codes as in Table 1.
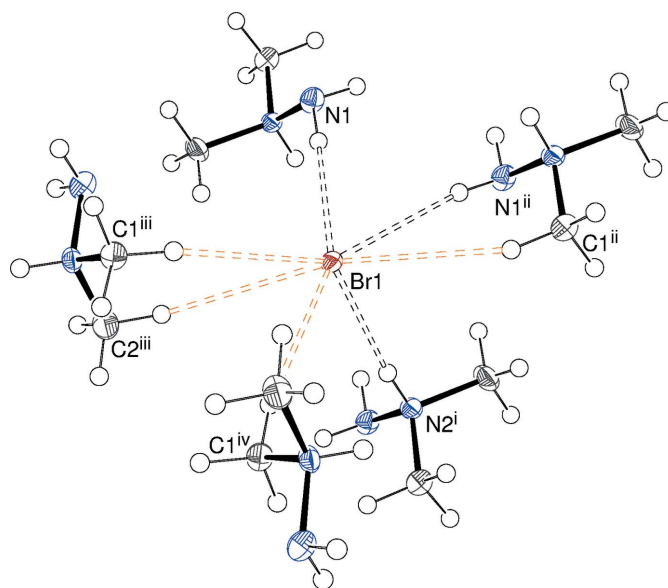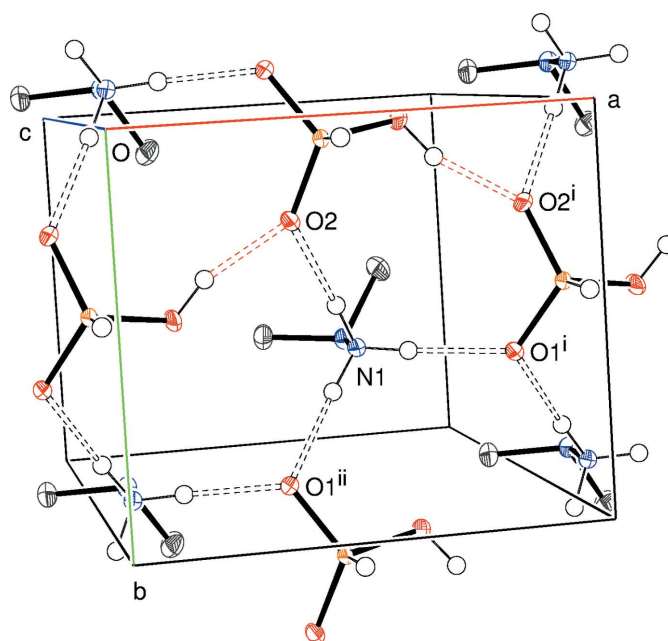

Figure 5
Partial packing diagram for (II), showing part of an (001) sheet. Symmetry codes as in Table 2.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_2H_9N_2^+\cdot Br^-$	$C_2H_9N_2^+\cdot H_2PO_3^-$
M_r	141.02	142.10
Crystal system, space group	Monoclinic, $I2/a$	Orthorhombic, $Pna2_1$
Temperature (K)	100	100
a, b, c (Å)	13.2423 (2), 5.1239 (1), 16.1839 (3)	8.0690 (2), 6.9970 (2), 11.7001 (6)
α, β, γ (°)	90, 94.838 (2), 90	90, 90, 90
V (Å^3)	1094.20 (3)	660.57 (4)
Z	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	7.36	0.35
Crystal size (mm)	$0.23 \times 0.09 \times 0.09$	$0.18 \times 0.18 \times 0.02$
Data collection		
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD
Absorption correction	Multi-scan (*CrystalClear*; Rigaku, 2012)	–
T_{min}, T_{max}	0.282, 0.557	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6485, 1258, 1224	5347, 1395, 1365
R_{int}	0.029	0.023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.051, 1.12	0.025, 0.065, 1.09
No. of reflections	1258	1395
No. of parameters	58	77
No. of restraints	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.50, −0.48	0.24, −0.28
Absolute structure	–	Refined as an inversion twin.
Absolute structure parameter	–	0.15 (14)

Computer programs: *CrystalClear* (Rigaku, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

safety measures must be put in place when handling this compound.

To prepare (I), aqueous solutions of UDMH (10 ml, 1.0 *M*) and hydrobromic acid (10 ml, 1.0 *M*) were mixed at room temperature to yield a colourless solution and colourless rods (to ∼1 mm in length) of (I) grew as the solvent evaporated in a watch glass. These crystals are extremely hygroscopic and should be immediately transferred to a desiccator for storage: if left in air, they absorb enough water to completely dissolve within an hour or two.

To prepare (II), aqueous solutions of UDMH (10 ml, 1.0 *M*) and phosphorus acid (10 ml, 1.0 *M*) were mixed at room temperature to yield a colourless solution and yellowish slabs of (II) grew as the increasingly viscous solvent slowly evaporated over several days in a watch glass. These crystals are hygroscopic and should be stored in a desiccator. IR: 2383 cm^{-1} (P—H stretch).

The IR spectra of UDMH, (I) and (II) are available as supporting information.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The N-bound H atoms in (I) were located in difference maps and their positions freely refined; those in (II) were relocated to idealized locations and refined as riding atoms. The O-bound H atom in (II) was located in a difference map and refined as riding, in its as-found relative position. The methyl H atoms were geometrically placed (C—H = 0.98 Å): the –CH$_3$ groups were allowed to rotate, but not to tip, to best fit the electron density. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied in all cases.

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supporting information

Different cation-protonation patterns in molecular salts of unsymmetrical dimethyhydrazine: $C_2H_9N_2$·Br and $C_2H_9N_2$·H_2PO_3

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Computing details

For both compounds, data collection: *CrystalClear* (Rigaku, 2012); cell refinement: *CrystalClear* (Rigaku, 2012); data reduction: *CrystalClear* (Rigaku, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) 1,1-Dimethylhydrazin-1-ium bromide

Crystal data

$C_2H_9N_2{}^+$·Br^-	$F(000) = 560$
$M_r = 141.02$	$D_x = 1.712$ Mg m^{-3}
Monoclinic, $I2/a$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.2423$ (2) Å	Cell parameters from 5743 reflections
$b = 5.1239$ (1) Å	$\theta = 2.5$–27.5°
$c = 16.1839$ (3) Å	$\mu = 7.36$ mm^{-1}
$\beta = 94.838$ (2)°	$T = 100$ K
$V = 1094.20$ (3) Å^3	Rod, colourless
$Z = 8$	$0.23 \times 0.09 \times 0.09$ mm

Data collection

Rigaku Mercury CCD diffractometer	1258 independent reflections
	1224 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2012)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.5°$
	$h = -17 \rightarrow 17$
$T_{min} = 0.282$, $T_{max} = 0.557$	$k = -6 \rightarrow 5$
6485 measured reflections	$l = -20 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.020$	Hydrogen site location: mixed
$wR(F^2) = 0.051$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.12$	$w = 1/[\sigma^2(F_o{}^2) + (0.0349P)^2 + 0.3874P]$
1258 reflections	where $P = (F_o{}^2 + 2F_c{}^2)/3$
58 parameters	$(\Delta/\sigma)_{max} = 0.001$
0 restraints	$\Delta\rho_{max} = 0.50$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Extinction correction: SHELXL2014
(Sheldrick, 2015),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0151 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.13506 (11)	0.3029 (3)	0.30499 (9)	0.0197 (3)
H1n	0.1888 (17)	0.204 (4)	0.3204 (13)	0.024*
H2n	0.1477 (17)	0.393 (3)	0.2599 (15)	0.024*
N2	0.13068 (10)	0.4851 (2)	0.37297 (8)	0.0170 (3)
H3n	0.1867 (17)	0.574 (4)	0.3765 (12)	0.020*
C1	0.11750 (14)	0.3372 (3)	0.45000 (11)	0.0191 (3)
H1a	0.1708	0.2047	0.4582	0.029*
H1b	0.0510	0.2519	0.4454	0.029*
H1c	0.1220	0.4571	0.4973	0.029*
C2	0.04544 (15)	0.6693 (3)	0.35325 (15)	0.0278 (4)
H2a	0.0567	0.7656	0.3025	0.042*
H2b	0.0416	0.7925	0.3992	0.042*
H2c	−0.0182	0.5715	0.3450	0.042*
Br1	0.17057 (2)	0.64136 (3)	0.12100 (2)	0.01501 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0198 (7)	0.0244 (6)	0.0150 (7)	0.0014 (6)	0.0030 (5)	0.0027 (5)
N2	0.0120 (6)	0.0147 (6)	0.0240 (7)	−0.0019 (5)	−0.0004 (5)	0.0017 (5)
C1	0.0195 (8)	0.0226 (8)	0.0151 (8)	−0.0015 (5)	0.0010 (6)	−0.0008 (5)
C2	0.0175 (9)	0.0173 (8)	0.0479 (12)	0.0030 (6)	−0.0014 (8)	0.0067 (7)
Br1	0.01199 (13)	0.01558 (14)	0.01745 (14)	−0.00069 (4)	0.00116 (7)	0.00263 (4)

Geometric parameters (Å, º)

N1—N2	1.4478 (19)	C1—H1a	0.98
N1—H1n	0.89 (2)	C1—H1b	0.98
N1—H2n	0.89 (2)	C1—H1c	0.98
N2—C1	1.482 (2)	C2—H2a	0.98
N2—C2	1.485 (2)	C2—H2b	0.98
N2—H3n	0.87 (2)	C2—H2c	0.98
N2—N1—H1n	103.6 (14)	H1a—C1—H1b	109.5
N2—N1—H2n	108.0 (12)	N2—C1—H1c	109.5

H1n—N1—H2n	108.8 (19)	H1a—C1—H1c	109.5
N1—N2—C1	108.93 (12)	H1b—C1—H1c	109.5
N1—N2—C2	108.97 (14)	N2—C2—H2a	109.5
C1—N2—C2	111.38 (14)	N2—C2—H2b	109.5
N1—N2—H3n	107.4 (13)	H2a—C2—H2b	109.5
C1—N2—H3n	111.9 (13)	N2—C2—H2c	109.5
C2—N2—H3n	108.1 (13)	H2a—C2—H2c	109.5
N2—C1—H1a	109.5	H2b—C2—H2c	109.5
N2—C1—H1b	109.5		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1n⋯Br1[i]	0.89 (2)	2.68 (3)	3.5666 (15)	170.7 (18)
N1—H2n⋯Br1	0.89 (2)	2.62 (2)	3.5117 (14)	175.0 (19)
N2—H3n⋯Br1[ii]	0.87 (2)	2.39 (2)	3.2490 (13)	173.3 (17)
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Symmetry codes: (i) $-x+1/2, -y+1/2, -z+1/2$; (ii) $-x+1/2, -y+3/2, -z+1/2$; (iii) $-x, y-1/2, -z+1/2$; (iv) $x, -y+3/2, z+1/2$.

(II) 2,2-Dimethylhydrazin-1-ium dihydrogen phosphite

Crystal data

$C_2H_9N_2^+ \cdot H_2PO_3^-$	$D_x = 1.429$ Mg m^{-3}
$M_r = 142.10$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $Pna2_1$	Cell parameters from 4031 reflections
$a = 8.0690$ (2) Å	$\theta = 3.4$–27.5°
$b = 6.9970$ (2) Å	$\mu = 0.35$ mm^{-1}
$c = 11.7001$ (6) Å	$T = 100$ K
$V = 660.57$ (4) Å^3	Plate, yellow
$Z = 4$	0.18 × 0.18 × 0.02 mm
$F(000) = 304$	

Data collection

Rigaku Mercury CCD diffractometer	$R_{int} = 0.023$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
5347 measured reflections	$h = -8 \rightarrow 10$
1395 independent reflections	$k = -8 \rightarrow 9$
1365 reflections with $I > 2\sigma(I)$	$l = -15 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.025$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.065$	
$S = 1.09$	Hydrogen site location: mixed
1395 reflections	H-atom parameters constrained
77 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.203P]$
1 restraint	where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.15 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.5416 (2)	0.5852 (2)	0.22552 (17)	0.0132 (4)
H1n	0.6455	0.5972	0.1962	0.016*
H2n	0.4779	0.6848	0.2016	0.016*
H3n	0.4960	0.4735	0.2011	0.016*
N2	0.5499 (2)	0.5853 (3)	0.34964 (17)	0.0145 (4)
C1	0.3807 (3)	0.5724 (3)	0.3936 (3)	0.0189 (5)
H1a	0.3169	0.6834	0.3677	0.028*
H1b	0.3832	0.5699	0.4773	0.028*
H1c	0.3286	0.4551	0.3652	0.028*
C2	0.6471 (3)	0.4186 (3)	0.3845 (2)	0.0206 (5)
H2a	0.7575	0.4255	0.3499	0.031*
H2b	0.5912	0.3018	0.3590	0.031*
H2c	0.6576	0.4169	0.4679	0.031*
P1	0.45797 (6)	0.05934 (7)	0.10615 (6)	0.01209 (15)
H1	0.4666	0.0529	−0.0064	0.015*
O1	0.35870 (18)	−0.1101 (2)	0.14409 (14)	0.0153 (3)
O2	0.39202 (17)	0.2526 (2)	0.13797 (14)	0.0165 (4)
O3	0.63746 (19)	0.0285 (2)	0.15307 (17)	0.0196 (4)
H1o	0.7059	0.1224	0.1417	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0099 (8)	0.0108 (8)	0.0189 (10)	0.0002 (6)	−0.0001 (7)	−0.0003 (7)
N2	0.0114 (9)	0.0142 (9)	0.0180 (11)	0.0005 (6)	−0.0007 (7)	−0.0007 (8)
C1	0.0124 (10)	0.0206 (11)	0.0236 (13)	−0.0007 (8)	0.0021 (10)	−0.0016 (9)
C2	0.0172 (11)	0.0209 (12)	0.0237 (13)	0.0050 (8)	−0.0028 (10)	0.0023 (10)
P1	0.0074 (2)	0.0095 (2)	0.0194 (3)	0.00031 (18)	0.0003 (3)	0.0004 (2)
O1	0.0097 (6)	0.0100 (7)	0.0263 (9)	−0.0005 (6)	0.0011 (6)	0.0013 (6)
O2	0.0097 (6)	0.0112 (7)	0.0286 (10)	0.0017 (6)	−0.0011 (6)	−0.0023 (6)
O3	0.0075 (6)	0.0127 (7)	0.0386 (10)	−0.0009 (6)	−0.0030 (7)	0.0040 (7)

Geometric parameters (Å, º)

N1—N2	1.454 (3)	C2—H2a	0.98
N1—H1n	0.91	C2—H2b	0.98
N1—H2n	0.91	C2—H2c	0.98
N1—H3n	0.91	P1—O1	1.4982 (15)
N2—C1	1.462 (3)	P1—O2	1.5003 (16)
N2—C2	1.463 (3)	P1—O3	1.5638 (16)
C1—H1a	0.98	P1—H1	1.32
C1—H1b	0.98	O3—H1o	0.8689
C1—H1c	0.98		
N2—N1—H1n	109.5	H1b—C1—H1c	109.5
N2—N1—H2n	109.5	N2—C2—H2a	109.5
H1n—N1—H2n	109.5	N2—C2—H2b	109.5
N2—N1—H3n	109.5	H2a—C2—H2b	109.5
H1n—N1—H3n	109.5	N2—C2—H2c	109.5
H2n—N1—H3n	109.5	H2a—C2—H2c	109.5
N1—N2—C1	107.94 (18)	H2b—C2—H2c	109.5
N1—N2—C2	107.62 (17)	O1—P1—O2	116.76 (9)
C1—N2—C2	110.69 (18)	O1—P1—O3	106.37 (9)
N2—C1—H1a	109.5	O2—P1—O3	111.46 (9)
N2—C1—H1b	109.5	O1—P1—H1	107.3
H1a—C1—H1b	109.5	O2—P1—H1	107.3
N2—C1—H1c	109.5	O3—P1—H1	107.3
H1a—C1—H1c	109.5	P1—O3—H1o	115.5

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1n···O1[i]	0.91	1.83	2.736 (2)	176
N1—H2n···O1[ii]	0.91	1.85	2.762 (2)	176
N1—H3n···O2	0.91	1.91	2.814 (2)	175
O3—H1o···O2[i]	0.87	1.74	2.568 (2)	159

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