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Three new quinuclidine-based structures: second harmonic generation response for 1,2-bis(1-azoniabicyclo[2.2.2]octan-3-ylidene)hydrazine dichloride

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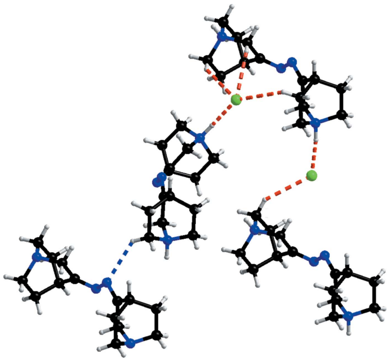
The crystal structures of three quinuclidine-based compounds, namely (1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine monohydrate, $C_7H_{13}N_3 \cdot H_2O$ (**1**), 1,2-bis(1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine, $C_{14}H_{22}N_4$ (**2**), and 1,2-bis(1-azoniabicyclo[2.2.2]octan-3-ylidene)hydrazine dichloride, $C_{14}H_{24}N_4^{2+} \cdot 2Cl^-$ (**3**), are reported. In the crystal structure of **1**, the quinuclidine-substituted hydrazine and water molecules are linked through N—H⋯O and O—H⋯N hydrogen bonds, forming a two-dimensional array. The compound crystallizes in the centrosymmetric space group $P2_1/c$. Compound **2** was refined in the space group *Pccn* and exhibits no hydrogen bonding. However, its hydrochloride form **3** crystallizes in the noncentrosymmetric space group *Pc*. It shows a three-dimensional network structure *via* intermolecular hydrogen bonding (N—H⋯C and N/C—H⋯Cl). Compound **3**, with its acentric structure, shows strong second harmonic activity.



1. Introduction

Hydrogen bonding plays an important role in the crystallization of molecules (Minkov *et al.*, 2015; Zick & Geiger, 2018; Swinton Darious *et al.*, 2018; Bekö *et al.*, 2014) and has a strong influence on phase transitions (Fortes *et al.*, 2014; Binns *et al.*, 2016). It is worth noting that not only strong N—H⋯O and O—H⋯O hydrogen bonds, but also weak C—H⋯O hydrogen bonds, are important in the formation of structural networks in crystals (Jelsch & Bibila Mayaya Bisseyou, 2017). As early as 1982, Taylor & Kennard (1982) provided evidence for the presence of dominant C—H⋯O interactions in crystals. Sarma & Desiraju (1986) pointed out that structures could be modified by manipulation of the hydrogen bonds in several planar aromatics. Not only hydrogen-bonding and Coulombic interactions play a significant role (Taylor, 2016; Gavezzotti & Lo Presti, 2016; Lo Presti, 2018), but weak hydrogen bonding has also attracted widespread attention in crystal packing or relative physicochemical properties (Nogueira *et al.*, 2015; Belkova *et al.*, 2016). Nevertheless, there is a debate on the importance of the interaction between a C—H⋯*X*-type (*X* = O, N and halogen) hydrogen bonds on the crystal packing (Amamou *et al.*, 2017; El Glaoui *et al.*, 2018; Ustabaş *et al.*, 2018). Hence, particular attention is paid to their roles when analyzing a crystal structure.

The well-known hydrazine-based molecules are of particular interest due to their ability to form both intra- and intermolecular hydrogen bonds (Sonar *et al.*, 2004; Duan *et al.*, 2005; Beckmann & Brooker, 2006). In this regard, we report

Table 1
Experimental details **[see Note 5]**.

	1	**2**	**3**
Crystal data			
Chemical formula	$C_7H_{13}N_3 \cdot H_2O$	$C_{14}H_{22}N_4$	$C_{14}H_{24}N_4^{2+} \cdot 2Cl^-$
M_r	157.22	246.36	319.27
Crystal system, space group	Monoclinic, *P*2$_1$/*c*	Orthorhombic, *Pccn*	Monoclinic, *Pc*
Temperature (K)	200	288	293
a, *b*, *c* (Å)	11.2687 (6), 8.3690 (5), 8.9974 (5)	19.7143 (13), 6.6047 (4), 9.9924 (6)	6.1699 (3), 12.5258 (7), 10.6570 (5)
α, β, γ (°)	90, 95.724 (5), 90	90, 90, 90	90, 103.023 (5), 90
V (Å^3)	844.29 (8)	1301.08 (14)	802.42 (7)
Z	4	4	2
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.09	0.08	0.40
Crystal size (mm)	0.38 × 0.26 × 0.20	0.35 × 0.25 × 0.2	0.3 × 0.25 × 0.2
Data collection			
Diffractometer	XtaLAB Synergy R, DW system, HyPix	XtaLAB Synergy R, DW system, HyPix	XtaLAB Synergy R, DW system, HyPix
Absorption correction	Multi-scan (North *et al.*, 1968)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)	Multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min}, T_{max}	0.974, 0.983	0.977, 0.985	0.887, 0.923
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8118, 2616, 1640	6797, 2033, 1216	5076, 4949, 2820
R_{int}	0.027	0.026	0.019
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.718	0.719	0.717
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.039, 0.097, 1.05	0.041, 0.112, 1.07	0.038, 0.097, 1.00
No. of reflections	2616	2033	4949
No. of parameters	116	82	182
No. of restraints	0	0	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.17	0.18, −0.16	0.28, −0.17
Absolute structure	–	–	Flack *x* determined using 986 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	–	0.02 (4)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *DIAMOND* (Brandenburg & Putz, 2000).

herein the structures of the hydrazine-based compounds (1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine monohydrate (**1**), (1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine (**2**) and 1,2-bis(1-azoniabicyclo[2.2.2]octan-3-ylidene)hydrazine dichloride (**3**). The differences in the hydrogen-bond patterns and the types of space groups are discussed. Second harmonic generation (SHG) response was further examined for the crystal with a noncentrosymmetric space group, *i.e.* **3**.

2. Experimental

2.1. Synthesis and crystallization

2.1.1. Synthesis of 1,2-bis(1-azoniabicyclo[2.2.2]octan-3-ylidene)hydrazine (BABYH) chloride. The synthesis of a Schiff base is usually conducted by refluxing the solution of an amine and a ketone or aldehyde (Vigato & Tamburini, 2004). We began the synthesis of compounds **1**, **2** and **3** with commercially available 3-quinuclidone hydrochloride, as shown in Fig. 1.

2.1.2. Synthesis of 3-quinuclidone. Commercially available 3-quinuclidone hydrochloride (100 g, 0.62 mol) was placed in a 1 l flask. NaOH (290 ml, 2 *M* in water) was added gradually to the flask at 0 °C, followed by Na_2CO_3 (6.56 g, 0.063 mol). The reaction mixture was stirred for 0.5 h and the crude product was extracted from the reaction mixture with dry dichloromethane (3 × 150 ml). The combined organic layers were dried with Na_2SO_4, filtered and concentrated. The resulting residue yielded 3-quinuclidone hydrochloride (77 g, yield 100%) as a white solid.

2.1.3. Synthesis of 1. 3-Quinuclidone (4.37 g, 0.035 mol) and N_2H_4 (2.5 ml, 80%) in water were placed in a 100 ml flask under a nitrogen atmosphere and heated at 120 °C under reflux overnight. The mixture was cooled in an ice bath for 3 h to yield white crystals, which were separated and subsequently washed with diethyl ether. The final compound, *i.e.* **1** (yield 3.9 g, 80%), was collected and further characterized by X-ray diffraction.

2.1.4. Synthesis of 2 and 3. Compound **1** (2 g, 0.014 mol) was dissolved in ethanol (20 ml) and the mixture was refluxed at 80 °C for 1 h. Crystals of **2** were obtained after the solvent had been evaporated under ambient conditions (Barton *et al.*, 1983). Compound **3** was obtained by acidification of compound **2** using a few drops of a 1 *M* HCl aqueous solution and was recrystallized by solvent evaporation from an aqueous solution.

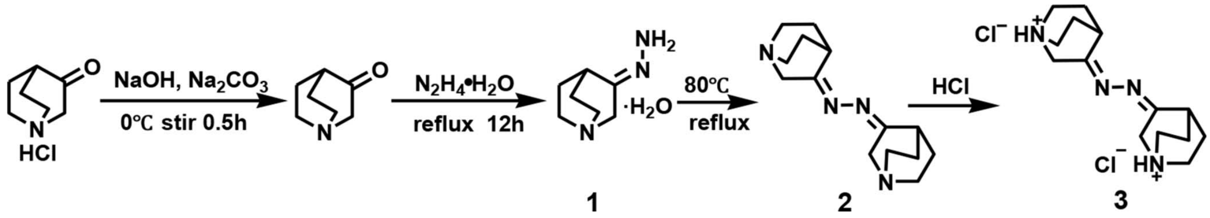


Figure 1
The synthesis route for the preparation of **1**, **2** and **3**.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms bonded to O and most N atoms were located in difference Fourier maps and refined freely. H atoms bonded to C atoms and to protonated N atoms were placed in idealized positions and refined as riders, with C—H = 0.97 (methylene) and 0.98 Å (methine and azonium). U_{iso} values for riding H atoms were set at $1.2U_{eq}$(C,N).

2.3. Second harmonic generation (SHG) measurement

The methods used for the SHG measurements have been described elsewhere (Zhang *et al.*, 2014). The SHG was conducted with an unexpanded laser beam at low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power and 10 Hz repetition rate). The instrument model was an Ins 1210058 (INSTEC Instruments), while the laser was a Vibrant 355 II (OPOTEK). The numerical values of the nonlinear optical coefficients for the SHG were determined by comparison with a KDP reference.

3. Results and discussion

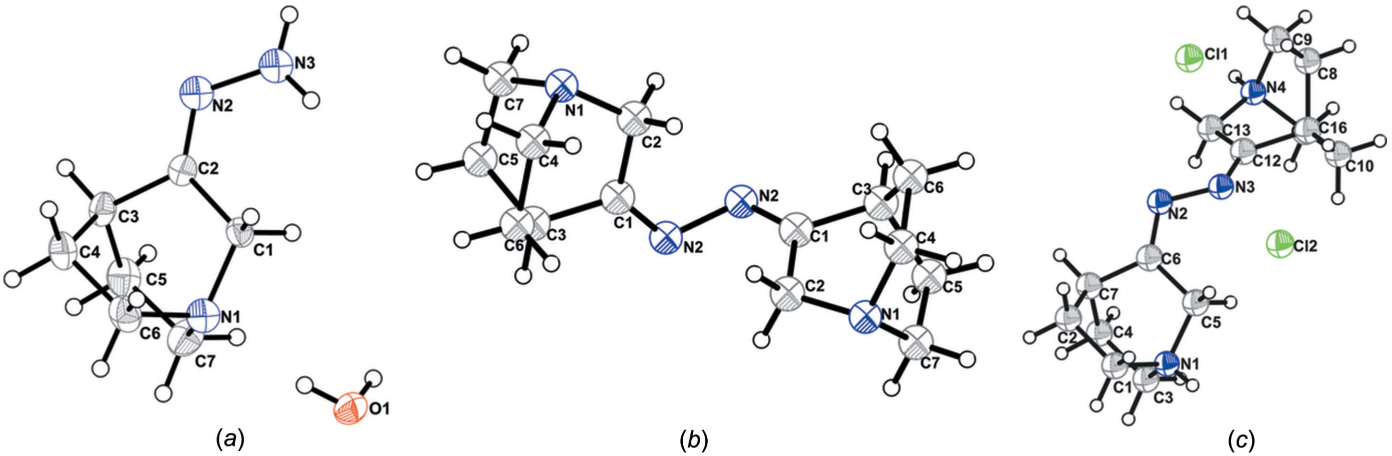
3.1. Crystal structure description

Compounds **1** and **2** crystallize in the centrosymmetric space groups $P2_1/c$ and $Pccn$, respectively, while compound **3** crystallizes in the noncentrosymmetric space group Pc (Table 1). As shown in Fig. 2, the contents of the asymmetric unit of **1** include a (1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine (ABYH) molecule and a water molecule. The ABYH molecule has a quinuclidine structure with a hydrazine group substituted at the *meta* position. The asymmetric unit of **2** is composed of one half of the BABYH molecule. The complete molecule was generated by a twofold axis crossing the N2—N2^{vi} bond [symmetry code: (vi) $-x+\frac{3}{2}, -y+\frac{1}{2}, z$]. Compound **3** consists of one protonated BABYH cation (*i.e.* [BABYH$_2$]$^+$) and two independent Cl$^-$ anions (Fig. 2) in the asymmetric unit. Full details of the bond lengths and angles are listed in the supporting information (Tables S1–S3). The hydrogen bonding has a significant influence on the molecular packing. Specifically, compound **1** crystallizes in the centrosymmetric space group $P2_1/c$ through intermolecular N—H···O and O—H···N hydrogen bonds, forming a two-dimensional (2D) layer structure *via* the amine group and the water network. Without the assistance of hydrogen bonding, compound **2** crystallizes in the orthorhombic space group $Pccn$. The presence of N—H···C and N/C—H···Cl interactions leads to compound **3**, which crystallizes in the

Table 2
Hydrogen-bond geometry (Å, °) for **1**.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.864 (18)	1.994 (19)	2.8207 (13)	159.9 (16)
O1—H2···N3^{ii}	0.874 (2)	2.042 (2)	2.915 (2)	176.05 (2)
N3—H3A···O1^{iv}	0.908 (17)	2.186 (17)	3.0517 (15)	159.3 (14)
N3—H3B···O1^{v}	0.898 (17)	2.212 (17)	3.0529 (15)	155.6 (13)

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



(*a*) (*b*) (*c*)

Figure 2
(*a*) The asymmetric unit of **1**, (*b*) the molecular structure of **2** and (*c*) the asymmetric unit of **3**, showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x+\frac{3}{2}, -y+\frac{1}{2}, z$.]

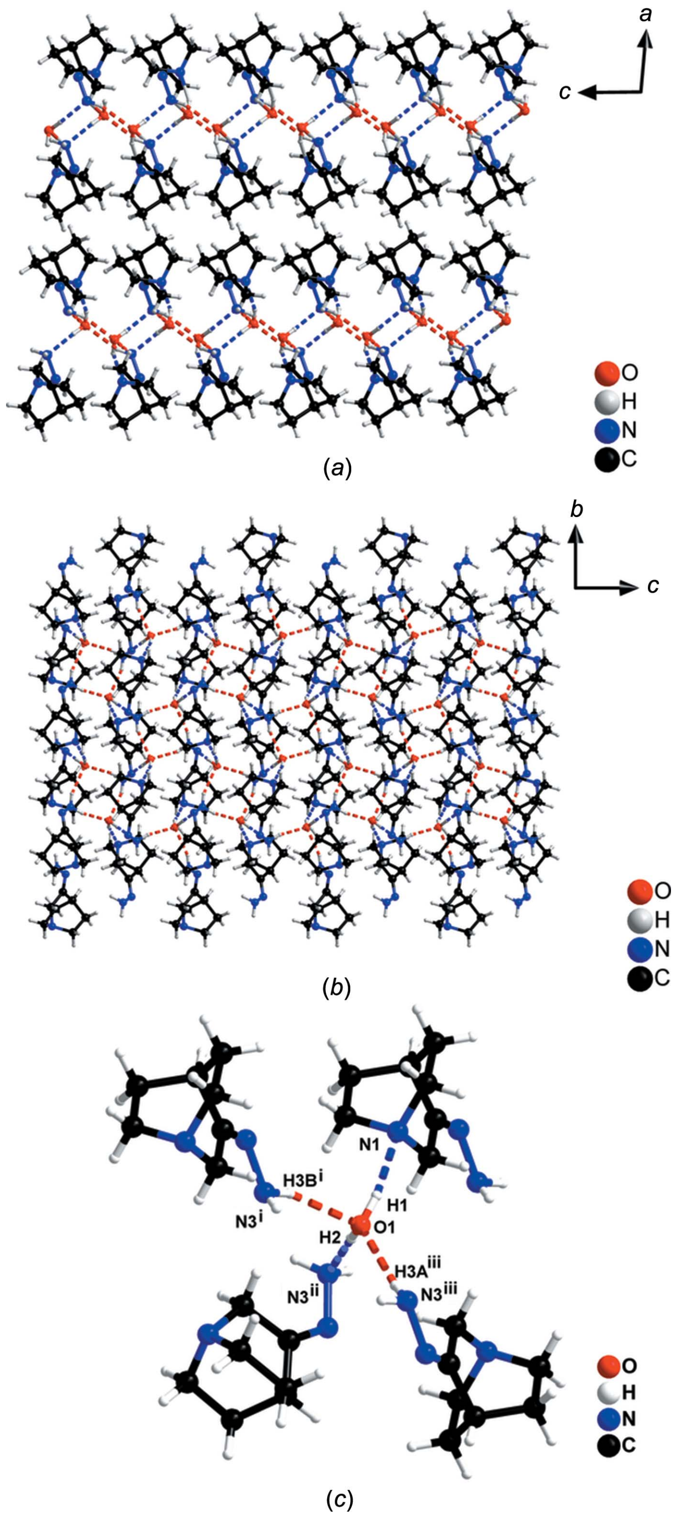


Figure 3
The 2D layer formed through intermolecular hydrogen bonds in **1**, viewed (*a*) along the *b* axis and (*b*) along the *a* axis. (*c*) The detailed hydrogen bonding, with intermolecular N—H···O and O—H···N hydrogen bonds indicated by red and blue dashed lines, respectively. [Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, -y, -z$; (iii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$.]

noncentrosymmetric space group *Pc*. The crystal structures are described below.

Table 3
Hydrogen-bond geometry (Å, °) for **3**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1^i—H1*A*^{i}···Cl2	0.98 (2)	2.027 (2)	3.007 (2)	177.90 (2)
N4^i—H4*C*^{i}···Cl1	0.98 (2)	2.069 (2)	3.043 (2)	172.42 (2)
C2^i—H2*B*^{i}···Cl2	0.97 (2)	2.852 (2)	3.657 (2)	141.00 (2)
C4^{ii}—H4*B*^{ii}···Cl1	0.97 (2)	2.888 (2)	3.737 (2)	146.75 (2)
C7^i—H7*A*^{i}···Cl2	0.97 (2)	2.893 (2)	3.697 (2)	140.87 (2)
C12^i—H12*A*^{i}···Cl2	0.97 (2)	2.906 (2)	3.684 (2)	137.92 (2)
C13—H13*B*···N3^{iii}	0.97 (2)	2.626 (2)	3.356 (2)	132.3 (2)

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

3.1.1. Crystal structure of (1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine monohydrate, 1

In the crystal structure of **1**, the ABYH and H_2O molecules are linked through N—H···O and O—H···N hydrogen bonds into a 2D array along the *bc* plane (Figs. 3*a* and 3*b*, and Table 2). As shown in Fig. 3(*c*), the water molecule interacts with the ABYH molecule through two types of hydrogen bonds and is embedded between the ABYH layers. Firstly, the amino N3 atoms act as donors and the water O atoms as acceptors in N—H···O hydrogen bonds (red dashed lines). The average hydrogen-bond length (N—H···O) is 3.0517 (15) Å. Secondly, the O atoms act as donors and form hydrogen bonds with N1 and N3^{ii}, as depicted in Fig. 3(*c*). It is worth noting that since the acceptors are derived from different sites on the ABYH molecule, the hydrogen-bond lengths are 2.8207 (13) and 2.915 (2) Å for O1—H1···N1 and O1—H2···N3^{ii}, respectively. The asymmetry of the ABYH molecule itself and the two different types of hydrogen bonds leads to compound **3**, which crystallizes in a monoclinic system with relatively low symmetry. The hydrogen-bond interactions in the regular sandwiched ABYH/water/ABYH structure seems to play a key role in achieving the packing characteristics and the higher stability of the structure (Etter *et al.*, 1990; Etter, 1990; Steiner, 2002).

3.1.2. Crystal structure of (1-azabicyclo[2.2.2]octan-3-ylidene)hydrazine, 2

As shown in Fig. 4, compound **2** exhibits the typical *s-trans E*,*E* configuration (Sanz *et al.*, 1999;

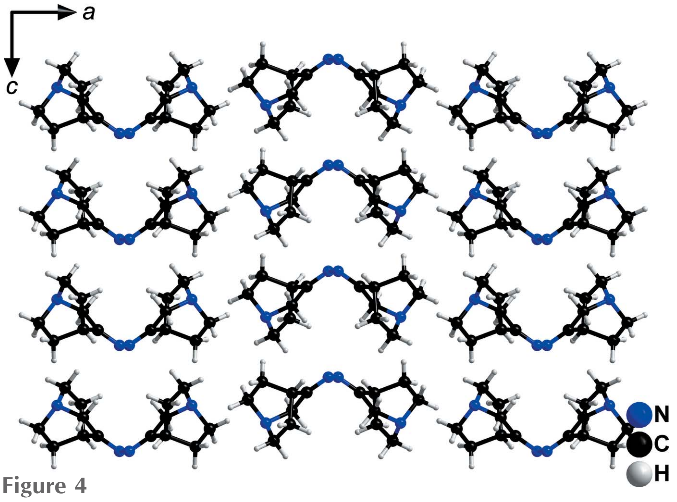


Figure 4
A packing view of **2** on the *ac* plane.

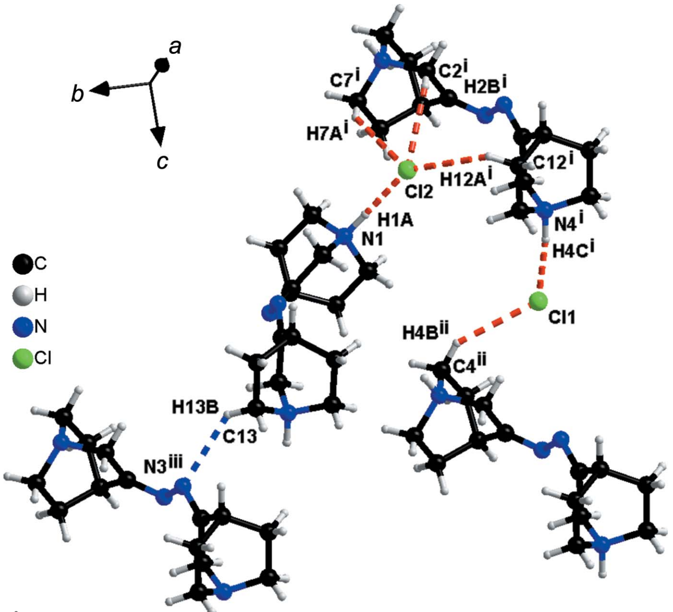


Figure 5
Part of the crystal structure of **3**, showing the hydrogen-bond information for N/C—H···Cl (red dashed lines) and C—H···N (blue dashed lines). [Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $x, -y+1, z+\frac{1}{2}$; (iii) $x, -y+2, z+\frac{1}{2}$.]

Saeed *et al.*, 2012; Ali *et al.*, 2011; Li & Han, 2016; Hsu *et al.*, 1993). Each molecular unit of compound **2** is related by a crystallographic twofold axis parallel to the *c* axis and a crystallographic glide plane perpendicular to the *a* axis between the N2 and N2$^{\rm i}$ atoms. Compound **2** crystallizes in the orthorhombic space group *Pccn*, which is higher in symmetry than **1** (space group $P2_1/c$). This could be explained by two facts: (i) the intermolecular interactions (hydrogen bonding) cause deviations from close packing and hence affect the crystal structures and properties at a subtle level (Prokopchuk *et al.*, 2019; Paufler, 2012). The absence of H atoms on the N atoms and no potential for hydrogen-bond interactions in the molecular stacking of **2** (Fig. 4) leads to a symmetrical arrangement during the molecular packing process. (ii) The centrosymmetric feature of **2** originates mainly from the molecular shape and van der Waals forces.

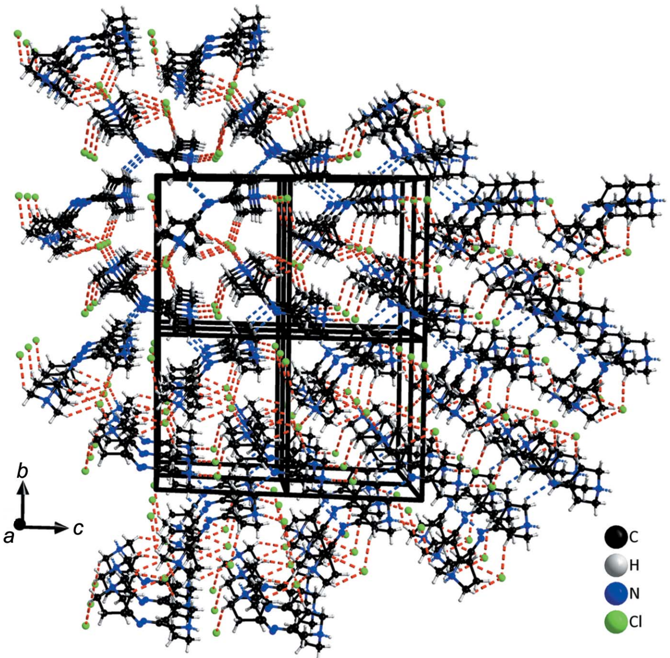


Figure 6
The 3D structure of **3** mediated by the intermolecular hydrogen bonding (dashed lines).

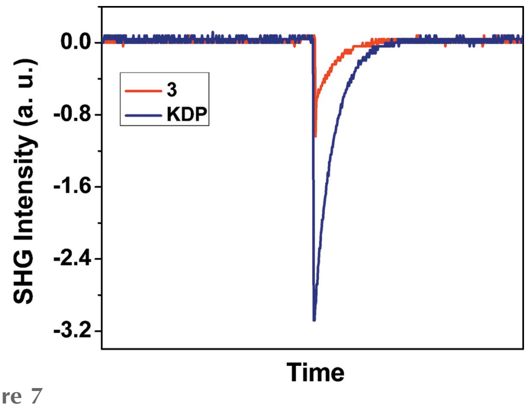


Figure 7
SHG response of **3** relative to KDP.

3.1.3. Crystal structure of 1,2-bis(1-azoniabicyclo[2.2.2]-octan-3-ylidene)hydrazine dichloride, 3.

Fig. 5 displays the hydrogen-bond information for N/C—H···Cl and C—H···N. Fig. 6 shows the crystal packing of **3**. The $[\mathrm{BABYH}_2]^+$ cations connect with each other through intermolecular hydrogen bonds (N—H···C and N/C—H···Cl) and form a regularly arranged three-dimensional (3D) network structure. There are three types of hydrogen bonds in the crystal structure; detailed information is given in Table 3. Firstly, the Cl1 atom bridges two quinine units through N/C—H···Cl hydrogen bonds, where Cl1 acts as an acceptor and N4 and C4 act as donors. The hydrogen-bond lengths are 3.043 (2) (N4$^{\rm i}$—H4$C^{\rm i}$···Cl1) and 3.737 (2) Å (C4$^{\rm ii}$—H4$B^{\rm ii}$···Cl1). Secondly, the Cl2 atom acts as an acceptor and forms hydrogen bonds with H1*A*, H7*A*, H2*B* and H12*A*. The third type of hydrogen bond is N—H···C involving atom C13; the H13*B*···N3$^{\rm iii}$ bond distance is 2.626 (2) Å. Compound **3** crystallizes in the noncentrosymmetric space group *Pc*, which is lower in symmetry than **1** and **2**. The hydrogen-bond stacking of **3** is obviously different from that of **1**. The asymmetry of **3** could be attributed to the diversity of hydrogen bonds. The Cl$^-$ anions bridge the cations and form the 3D structure, resulting in significant polarization. The asymmetry properties of these compounds were further investigated by the measurement of second harmonic generation (SHG) response. To measure the relative value of the SHG efficiencies, potassium dihydrogen phosphate ($\mathrm{KH_2PO_4}$, KDP) powder was chosen as the reference sample. KDP is famous for its excellent nonlinear optical properties, showing strong SHG properties (Shkir *et al.*, 2013). It has been widely developed for powerful laser systems (De Yoreo *et al.*, 2002). Since the nonlinear optical properties result from the dipole moment, the SHG signal is a sign of the polarity of the material. Here, the sample powders were placed under a pulsed laser at 1064 nm. As shown in Fig. 7, the measured

SHG intensity of compound **3** is roughly 0.3 times that of KDP at room temperature. Unsurprisingly, **1** and **2** show no significant SHG signal.

4. Conclusion

In summary, the title compounds have been synthesized through a catalyst-free route. Hydrogen bonding plays a crucial role in the molecular packing. Compound **1** crystallized in the centrosymmetric space group $P2_1/c$ *via* robust hydrogen bonding (N—H···O and O—H···N) and formed a 2D sandwich structure. Compound **2** crystallizes in the space group *Pccn* without hydrogen-bonding assistance. Compound **3** shows a 3D network structure *via* intermolecular hydrogen bonds (N—H···C and N/C—H···Cl) and crystallizes in the noncentrosymmetric space group *Pc*. Analysis of the hydrogen-bond interactions allows us to understand the symmetry properties of the crystal structures.

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supporting information

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Three new quinuclidine-based structures: second harmonic generation response for 1,2-bis(1-azoniabicyclo[2.2.2]octan-3-ylidene)hydrazine dichloride

Liang Qiao, Xiao-Gang Chen, Ji-Xing Gao and Yong Ai

Computing details

For all structures, data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2000); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

(1-Azabicyclo[2.2.2]oct-3-ylidene)hydrazine monohydrate (P21C)

Crystal data

$C_7H_{13}N_3{\cdot}H_2O$
$M_r = 157.22$
Monoclinic, $P2_1/c$
$a = 11.2687$ (6) Å
$b = 8.3690$ (5) Å
$c = 8.9974$ (5) Å
$\beta = 95.724$ (5)°
$V = 844.29$ (8) Å^3
$Z = 4$
$F(000) = 344$
$D_x = 1.237$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3399 reflections
$\theta = 3.0$–$30.3°$
$\mu = 0.09$ mm^{-1}
$T = 200$ K
Bar, colorless
0.38 × 0.26 × 0.20 mm

Data collection

XtaLAB Synergy R, DW system, HyPix diffractometer
Radiation source: Rotating-anode X-ray tube
ω scans
Absorption correction: multi-scan (North *et al.*, 1968)
$T_{\min} = 0.974$, $T_{\max} = 0.983$
8118 measured reflections
2616 independent reflections
1640 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 30.7°$, $\theta_{\min} = 3.0°$
$h = -16{\rightarrow}12$
$k = -12{\rightarrow}9$
$l = -12{\rightarrow}11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.097$
$S = 1.05$
2616 reflections
116 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.2373P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b)
Extinction coefficient: 0.012 (3)

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}
H2	0.5044 (16)	0.275 (2)	0.345 (2)	0.057 (5)*
H1	0.3994 (16)	0.275 (2)	0.4087 (19)	0.048 (5)*
H3A	0.4201 (14)	0.838 (2)	0.3883 (19)	0.040 (4)*
H3B	0.3984 (13)	0.994 (2)	0.3108 (17)	0.040 (4)*
C7	0.24509 (12)	0.36947 (17)	0.18145 (15)	0.0354 (3)
H7A	0.2078	0.2649	0.1747	0.042*
H7B	0.3218	0.3610	0.1419	0.042*
C6	0.14730 (11)	0.43570 (17)	0.39880 (15)	0.0331 (3)
H6A	0.1599	0.4674	0.5029	0.040*
H6B	0.1067	0.3334	0.3940	0.040*
C4	0.16618 (12)	0.48901 (17)	0.08594 (14)	0.0328 (3)
H4A	0.2082	0.5280	0.0042	0.039*
H4B	0.0934	0.4370	0.0442	0.039*
C5	0.06742 (11)	0.56098 (16)	0.31129 (15)	0.0318 (3)
H5A	−0.0061	0.5115	0.2686	0.038*
H5B	0.0475	0.6460	0.3777	0.038*
C3	0.13621 (10)	0.62896 (15)	0.18676 (13)	0.0265 (3)
H3	0.0893	0.7108	0.1293	0.032*
C2	0.25161 (10)	0.69677 (14)	0.25798 (12)	0.0227 (2)
C1	0.32424 (10)	0.57396 (14)	0.34956 (13)	0.0237 (3)
H1A	0.4022	0.5643	0.3135	0.028*
H1B	0.3353	0.6081	0.4530	0.028*
N3	0.39511 (10)	0.88691 (14)	0.30080 (13)	0.0291 (2)
N1	0.26369 (9)	0.41798 (12)	0.33943 (11)	0.0242 (2)
O1	0.46566 (9)	0.22272 (11)	0.40879 (11)	0.0315 (2)
N2	0.28043 (9)	0.84209 (12)	0.23735 (11)	0.0270 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C7	0.0380 (7)	0.0352 (8)	0.0314 (7)	0.0067 (5)	−0.0044 (5)	−0.0114 (5)
C6	0.0278 (7)	0.0388 (7)	0.0335 (7)	−0.0056 (5)	0.0066 (5)	0.0084 (5)
C4	0.0320 (7)	0.0428 (8)	0.0225 (6)	−0.0009 (5)	−0.0029 (5)	−0.0042 (5)
C5	0.0211 (6)	0.0397 (8)	0.0351 (7)	−0.0011 (5)	0.0053 (5)	0.0004 (5)
C3	0.0213 (6)	0.0317 (7)	0.0256 (6)	0.0030 (4)	−0.0018 (4)	0.0030 (5)
C2	0.0225 (6)	0.0261 (6)	0.0199 (6)	0.0016 (4)	0.0040 (4)	0.0011 (4)
C1	0.0208 (6)	0.0246 (6)	0.0249 (6)	−0.0024 (4)	−0.0011 (4)	0.0020 (4)
N3	0.0306 (6)	0.0242 (6)	0.0327 (6)	−0.0046 (4)	0.0046 (4)	0.0007 (4)
N1	0.0227 (5)	0.0245 (5)	0.0247 (5)	−0.0021 (4)	−0.0007 (4)	0.0002 (4)

O1	0.0310 (5)	0.0271 (5)	0.0360 (5)	0.0035 (4)	0.0020 (4)	0.0067 (4)
N2	0.0279 (5)	0.0275 (6)	0.0260 (5)	0.0010 (4)	0.0045 (4)	0.0026 (4)

Geometric parameters (Å, º)

C7—N1	1.4730 (16)	C5—H5B	0.9700
C7—C4	1.5419 (18)	C3—C2	1.5025 (16)
C7—H7A	0.9700	C3—H3	0.9800
C7—H7B	0.9700	C2—N2	1.2771 (16)
C6—N1	1.4722 (16)	C2—C1	1.5068 (16)
C6—C5	1.5453 (18)	C1—N1	1.4716 (15)
C6—H6A	0.9700	C1—H1A	0.9700
C6—H6B	0.9700	C1—H1B	0.9700
C4—C3	1.5394 (18)	N3—N2	1.4106 (15)
C4—H4A	0.9700	N3—H3A	0.908 (17)
C4—H4B	0.9700	N3—H3B	0.898 (17)
C5—C3	1.5341 (17)	O1—H2	0.87 (2)
C5—H5A	0.9700	O1—H1	0.864 (18)
N1—C7—C4	112.18 (10)	C2—C3—C5	107.91 (10)
N1—C7—H7A	109.2	C2—C3—C4	107.89 (9)
C4—C7—H7A	109.2	C5—C3—C4	107.74 (10)
N1—C7—H7B	109.2	C2—C3—H3	111.0
C4—C7—H7B	109.2	C5—C3—H3	111.0
H7A—C7—H7B	107.9	C4—C3—H3	111.0
N1—C6—C5	112.22 (10)	N2—C2—C3	121.30 (11)
N1—C6—H6A	109.2	N2—C2—C1	126.65 (11)
C5—C6—H6A	109.2	C3—C2—C1	112.05 (10)
N1—C6—H6B	109.2	N1—C1—C2	110.36 (9)
C5—C6—H6B	109.2	N1—C1—H1A	109.6
H6A—C6—H6B	107.9	C2—C1—H1A	109.6
C3—C4—C7	108.27 (10)	N1—C1—H1B	109.6
C3—C4—H4A	110.0	C2—C1—H1B	109.6
C7—C4—H4A	110.0	H1A—C1—H1B	108.1
C3—C4—H4B	110.0	N2—N3—H3A	115.0 (10)
C7—C4—H4B	110.0	N2—N3—H3B	109.4 (10)
H4A—C4—H4B	108.4	H3A—N3—H3B	110.9 (14)
C3—C5—C6	108.22 (10)	C1—N1—C6	108.21 (9)
C3—C5—H5A	110.1	C1—N1—C7	108.95 (10)
C6—C5—H5A	110.1	C6—N1—C7	109.37 (10)
C3—C5—H5B	110.1	H2—O1—H1	103.7 (16)
C6—C5—H5B	110.1	C2—N2—N3	115.49 (10)
H5A—C5—H5B	108.4		
N1—C7—C4—C3	2.85 (15)	N2—C2—C1—N1	−176.92 (11)
N1—C6—C5—C3	0.10 (15)	C3—C2—C1—N1	2.16 (13)
C6—C5—C3—C2	−56.98 (13)	C2—C1—N1—C6	−60.83 (12)
C6—C5—C3—C4	59.28 (13)	C2—C1—N1—C7	58.00 (12)

C7—C4—C3—C2	55.23 (13)	C5—C6—N1—C1	59.56 (13)
C7—C4—C3—C5	−61.04 (13)	C5—C6—N1—C7	−59.00 (14)
C5—C3—C2—N2	−123.94 (12)	C4—C7—N1—C1	−60.92 (13)
C4—C3—C2—N2	119.90 (12)	C4—C7—N1—C6	57.18 (14)
C5—C3—C2—C1	56.93 (13)	C3—C2—N2—N3	−175.16 (10)
C4—C3—C2—C1	−59.23 (12)	C1—C2—N2—N3	3.84 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.864 (18)	1.994 (19)	2.8207 (13)	159.9 (16)
O1—H2···N3^{i}	0.874 (2)	2.042 (2)	2.915 (2)	176.05 (2)
N3—H3*A*···O1^{ii}	0.908 (17)	2.186 (17)	3.0517 (15)	159.3 (14)
N3—H3*B*···O1^{iii}	0.898 (17)	2.212 (17)	3.0529 (15)	155.6 (13)

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

1,2-Bis(1-azabicyclo[2.2.2]oct-3-ylidene)hydrazine (PCCN)

Crystal data

$C_{14}H_{22}N_4$
M_r = 246.36
Orthorhombic, *Pccn*
a = 19.7143 (13) Å
b = 6.6047 (4) Å
c = 9.9924 (6) Å
V = 1301.08 (14) Å^3
Z = 4
F(000) = 536
D_x = 1.258 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2940 reflections
θ = 3.2–30.6°
μ = 0.08 mm^{-1}
T = 288 K
Bar, colorless
0.35 × 0.25 × 0.2 mm

Data collection

XtaLAB Synergy R, DW system, HyPix diffractometer
Radiation source: Rotating-anode X-ray tube
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)
T_{min} = 0.977, T_{max} = 0.985
6797 measured reflections
2033 independent reflections
1216 reflections with *I* > 2*σ*(*I*)
R_{int} = 0.026
θ_{max} = 30.7°, θ_{min} = 3.3°
h = −28→23
k = −7→9
l = −11→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.112
S = 1.07
2033 reflections
82 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.2267P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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	0.58882 (5)	0.18453 (15)	0.29148 (11)	0.0438 (3)
N2	0.73834 (5)	0.14848 (15)	0.07517 (10)	0.0431 (3)
C1	0.65099 (6)	0.27017 (19)	0.23467 (13)	0.0416 (3)
H1A	0.6811	0.3114	0.3064	0.050*
H1B	0.6399	0.3892	0.1822	0.050*
C2	0.68635 (6)	0.11736 (17)	0.14723 (11)	0.0363 (3)
C3	0.65173 (6)	−0.08475 (18)	0.15064 (13)	0.0420 (3)
H3	0.6763	−0.1850	0.0970	0.050*
C4	0.64643 (8)	−0.1510 (2)	0.29696 (15)	0.0524 (4)
H4A	0.6227	−0.2793	0.3028	0.063*
H4B	0.6914	−0.1682	0.3345	0.063*
C5	0.57970 (7)	−0.0515 (2)	0.09707 (14)	0.0498 (4)
H5A	0.5814	−0.0097	0.0041	0.060*
H5B	0.5540	−0.1764	0.1026	0.060*
C6	0.54573 (7)	0.1127 (2)	0.18161 (15)	0.0535 (4)
H6A	0.5342	0.2263	0.1244	0.064*
H6B	0.5039	0.0594	0.2185	0.064*
C7	0.60774 (7)	0.0112 (2)	0.37512 (13)	0.0509 (4)
H7A	0.5670	−0.0483	0.4128	0.061*
H7B	0.6357	0.0582	0.4487	0.061*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0405 (6)	0.0480 (6)	0.0428 (6)	0.0003 (4)	0.0046 (5)	−0.0086 (5)
N2	0.0359 (6)	0.0513 (6)	0.0420 (6)	−0.0056 (4)	0.0000 (4)	−0.0048 (5)
C1	0.0450 (7)	0.0392 (6)	0.0407 (7)	−0.0025 (5)	0.0029 (6)	−0.0052 (5)
C2	0.0344 (6)	0.0419 (6)	0.0326 (6)	−0.0019 (5)	−0.0029 (5)	−0.0044 (5)
C3	0.0397 (7)	0.0411 (6)	0.0452 (7)	−0.0032 (5)	0.0052 (5)	−0.0112 (5)
C4	0.0537 (8)	0.0466 (7)	0.0569 (9)	0.0003 (6)	−0.0019 (7)	0.0061 (6)
C5	0.0435 (8)	0.0616 (8)	0.0443 (7)	−0.0109 (6)	−0.0030 (6)	−0.0129 (6)
C6	0.0375 (7)	0.0637 (9)	0.0593 (9)	0.0055 (6)	−0.0071 (6)	−0.0082 (7)
C7	0.0587 (9)	0.0569 (8)	0.0369 (7)	−0.0109 (6)	0.0026 (6)	0.0003 (6)

Geometric parameters (Å, º)

N1—C1	1.4643 (15)	C3—H3	0.9800
N1—C7	1.4656 (17)	C4—C7	1.5294 (19)
N1—C6	1.4670 (17)	C4—H4A	0.9700

N2—C2	1.2693 (16)	C4—H4B	0.9700
N2—N2^{i}	1.418 (2)	C5—C6	1.5291 (19)
C1—C2	1.5060 (16)	C5—H5A	0.9700
C1—H1A	0.9700	C5—H5B	0.9700
C1—H1B	0.9700	C6—H6A	0.9700
C2—C3	1.4996 (16)	C6—H6B	0.9700
C3—C4	1.5296 (19)	C7—H7A	0.9700
C3—C5	1.5335 (18)	C7—H7B	0.9700
C1—N1—C7	108.05 (10)	C7—C4—H4B	109.9
C1—N1—C6	108.64 (10)	C3—C4—H4B	109.9
C7—N1—C6	108.75 (10)	H4A—C4—H4B	108.3
C2—N2—N2^{i}	114.53 (11)	C6—C5—C3	108.32 (10)
N1—C1—C2	110.70 (10)	C6—C5—H5A	110.0
N1—C1—H1A	109.5	C3—C5—H5A	110.0
C2—C1—H1A	109.5	C6—C5—H5B	110.0
N1—C1—H1B	109.5	C3—C5—H5B	110.0
C2—C1—H1B	109.5	H5A—C5—H5B	108.4
H1A—C1—H1B	108.1	N1—C6—C5	112.91 (11)
N2—C2—C3	121.63 (11)	N1—C6—H6A	109.0
N2—C2—C1	126.47 (11)	C5—C6—H6A	109.0
C3—C2—C1	111.88 (10)	N1—C6—H6B	109.0
C2—C3—C4	107.90 (10)	C5—C6—H6B	109.0
C2—C3—C5	106.63 (11)	H6A—C6—H6B	107.8
C4—C3—C5	108.14 (11)	N1—C7—C4	112.50 (10)
C2—C3—H3	111.3	N1—C7—H7A	109.1
C4—C3—H3	111.3	C4—C7—H7A	109.1
C5—C3—H3	111.3	N1—C7—H7B	109.1
C7—C4—C3	108.79 (11)	C4—C7—H7B	109.1
C7—C4—H4A	109.9	H7A—C7—H7B	107.8
C3—C4—H4A	109.9		

Symmetry code: (i) $-x+3/2, -y+1/2, z$.

1,2-Bis(1-azoniabicyclo[2.2.2]oct-3-ylidene)hydrazine dichloride (PC)

Crystal data

$C_{14}H_{24}N_4^{2+}\cdot 2Cl^-$
$M_r = 319.27$
Monoclinic, *Pc*
$a = 6.1699$ (3) Å
$b = 12.5258$ (7) Å
$c = 10.6570$ (5) Å
$\beta = 103.023$ (5)°
$V = 802.42$ (7) Å^3
$Z = 2$

$F(000) = 340$
$D_x = 1.321$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2739 reflections
$\theta = 3.3$–28.9°
$\mu = 0.40$ mm^{-1}
$T = 293$ K
Bar, colorless
0.3 × 0.25 × 0.2 mm

Data collection

XtaLAB Synergy R, DW system, HyPix diffractometer
Radiation source: Rotating-anode X-ray tube
ω scans
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)
$T_{\min} = 0.887$, $T_{\max} = 0.923$
5076 measured reflections
4949 independent reflections
2820 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.019$
$\theta_{\max} = 30.6°$, $\theta_{\min} = 2.6°$
$h = -7 \rightarrow 8$
$k = -17 \rightarrow 13$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.097$
$S = 1.00$
4949 reflections
182 parameters
2 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.012 (3)
Absolute structure: Flack x determined using 986 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.02 (4)

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 (Å^2)

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
C1	0.8805 (5)	0.8659 (2)	1.0231 (3)	0.0406 (7)
H1A	0.8086	0.8278	1.0817	0.049*
H1B	0.9687	0.9231	1.0706	0.049*
C2	1.0310 (4)	0.7901 (3)	0.9705 (2)	0.0418 (7)
H2A	1.0183	0.7186	1.0031	0.050*
H2B	1.1847	0.8128	0.9985	0.050*
C3	0.8185 (5)	0.9758 (2)	0.8280 (3)	0.0435 (7)
H3A	0.9037	1.0336	0.8760	0.052*
H3B	0.7064	1.0066	0.7588	0.052*
C4	0.9719 (4)	0.9037 (3)	0.7722 (3)	0.0448 (7)
H4A	1.1231	0.9305	0.7964	0.054*
H4B	0.9262	0.9038	0.6789	0.054*
C5	0.5723 (4)	0.8252 (2)	0.8403 (2)	0.0347 (6)
H5A	0.4583	0.8556	0.7719	0.042*
H5B	0.5001	0.7837	0.8960	0.042*
C6	0.7243 (4)	0.7553 (2)	0.7845 (2)	0.0289 (5)
C7	0.9630 (4)	0.7898 (2)	0.8229 (2)	0.0332 (6)
H7A	1.0586	0.7419	0.7865	0.040*

C8	0.0225 (4)	0.7195 (2)	0.4151 (3)	0.0416 (7)
H8A	−0.1350	0.7125	0.3767	0.050*
H8B	0.0465	0.7882	0.4581	0.050*
C9	0.1537 (5)	0.7139 (3)	0.3112 (3)	0.0539 (9)
H9A	0.0527	0.7047	0.2279	0.065*
H9B	0.2347	0.7800	0.3095	0.065*
C10	0.0605 (4)	0.5227 (2)	0.4428 (3)	0.0413 (7)
H10A	0.1124	0.4652	0.5030	0.050*
H10B	−0.0969	0.5120	0.4066	0.050*
C11	0.1869 (5)	0.5209 (3)	0.3358 (3)	0.0561 (9)
H11A	0.2893	0.4610	0.3483	0.067*
H11B	0.0833	0.5120	0.2533	0.067*
C12	0.3415 (4)	0.6441 (2)	0.5650 (2)	0.0290 (6)
C13	0.4718 (4)	0.6380 (3)	0.4621 (2)	0.0421 (7)
H13A	0.5560	0.7032	0.4609	0.051*
H13B	0.5755	0.5787	0.4790	0.051*
C14	0.0964 (4)	0.6299 (2)	0.5133 (2)	0.0310 (6)
H14A	0.0155	0.6329	0.5825	0.037*
N1	0.7083 (3)	0.91179 (18)	0.9153 (2)	0.0331 (5)
H1C	0.6105	0.9588	0.9511	0.040*
N4	0.3130 (3)	0.6228 (2)	0.33635 (19)	0.0408 (6)
H4C	0.3959	0.6201	0.2681	0.049*
N2	0.6605 (3)	0.67783 (19)	0.70772 (19)	0.0336 (5)
N3	0.4259 (3)	0.66326 (18)	0.68247 (19)	0.0329 (5)
Cl1	0.57596 (10)	0.63584 (7)	0.12698 (7)	0.05067 (19)
Cl2	0.39849 (11)	0.05252 (7)	0.02162 (8)	0.0565 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0421 (13)	0.0470 (17)	0.0306 (12)	0.0046 (13)	0.0036 (10)	−0.0034 (12)
C2	0.0383 (13)	0.0460 (18)	0.0362 (13)	0.0112 (12)	−0.0020 (11)	−0.0062 (12)
C3	0.0434 (14)	0.0315 (15)	0.0535 (15)	−0.0041 (12)	0.0065 (12)	0.0052 (13)
C4	0.0400 (14)	0.0500 (18)	0.0471 (14)	−0.0119 (12)	0.0155 (11)	−0.0021 (13)
C5	0.0276 (11)	0.0365 (14)	0.0401 (12)	−0.0016 (10)	0.0077 (9)	−0.0059 (11)
C6	0.0308 (11)	0.0319 (13)	0.0238 (9)	0.0017 (10)	0.0054 (8)	0.0012 (10)
C7	0.0250 (11)	0.0392 (14)	0.0346 (11)	−0.0003 (10)	0.0049 (9)	−0.0104 (10)
C8	0.0325 (12)	0.0429 (17)	0.0473 (14)	0.0025 (11)	0.0050 (11)	0.0019 (13)
C9	0.0484 (15)	0.070 (2)	0.0439 (14)	0.0022 (14)	0.0123 (12)	0.0215 (14)
C10	0.0423 (14)	0.0378 (16)	0.0424 (13)	−0.0092 (12)	0.0069 (11)	−0.0051 (13)
C11	0.0610 (17)	0.058 (2)	0.0529 (15)	−0.0045 (15)	0.0201 (13)	−0.0237 (14)
C12	0.0316 (11)	0.0280 (13)	0.0286 (10)	−0.0022 (9)	0.0095 (9)	−0.0016 (9)
C13	0.0295 (12)	0.069 (2)	0.0278 (11)	0.0014 (12)	0.0066 (10)	−0.0017 (12)
C14	0.0282 (11)	0.0377 (15)	0.0283 (11)	−0.0048 (10)	0.0091 (9)	−0.0034 (10)
N1	0.0347 (10)	0.0277 (11)	0.0368 (10)	0.0020 (9)	0.0081 (8)	−0.0063 (9)
N4	0.0351 (10)	0.0651 (16)	0.0244 (9)	−0.0006 (10)	0.0116 (8)	−0.0037 (10)
N2	0.0297 (10)	0.0379 (13)	0.0330 (10)	−0.0034 (9)	0.0064 (8)	−0.0038 (9)
N3	0.0323 (9)	0.0351 (12)	0.0316 (9)	−0.0069 (9)	0.0081 (8)	−0.0034 (9)

Cl1	0.0489 (3)	0.0668 (5)	0.0401 (3)	−0.0099 (3)	0.0179 (2)	0.0007 (3)
Cl2	0.0476 (3)	0.0573 (4)	0.0599 (4)	0.0158 (3)	0.0020 (3)	−0.0226 (4)

Geometric parameters (Å, º)

C1—N1	1.493 (3)	C8—H8A	0.9700
C1—C2	1.521 (4)	C8—H8B	0.9700
C1—H1A	0.9700	C9—N4	1.490 (4)
C1—H1B	0.9700	C9—H9A	0.9700
C2—C7	1.534 (3)	C9—H9B	0.9700
C2—H2A	0.9700	C10—C11	1.519 (4)
C2—H2B	0.9700	C10—C14	1.530 (4)
C3—N1	1.502 (4)	C10—H10A	0.9700
C3—C4	1.522 (4)	C10—H10B	0.9700
C3—H3A	0.9700	C11—N4	1.494 (4)
C3—H3B	0.9700	C11—H11A	0.9700
C4—C7	1.532 (4)	C11—H11B	0.9700
C4—H4A	0.9700	C12—N3	1.266 (3)
C4—H4B	0.9700	C12—C14	1.499 (3)
C5—N1	1.488 (3)	C12—C13	1.500 (3)
C5—C6	1.501 (4)	C13—N4	1.484 (3)
C5—H5A	0.9700	C13—H13A	0.9700
C5—H5B	0.9700	C13—H13B	0.9700
C6—N2	1.273 (3)	C14—H14A	0.9800
C6—C7	1.501 (3)	N1—H1C	0.9800
C7—H7A	0.9800	N4—H4C	0.9800
C8—C9	1.514 (4)	N2—N3	1.423 (3)
C8—C14	1.532 (4)		
N1—C1—C2	110.2 (2)	N4—C9—H9A	109.6
N1—C1—H1A	109.6	C8—C9—H9A	109.6
C2—C1—H1A	109.6	N4—C9—H9B	109.6
N1—C1—H1B	109.6	C8—C9—H9B	109.6
C2—C1—H1B	109.6	H9A—C9—H9B	108.2
H1A—C1—H1B	108.1	C11—C10—C14	109.8 (2)
C1—C2—C7	109.3 (2)	C11—C10—H10A	109.7
C1—C2—H2A	109.8	C14—C10—H10A	109.7
C7—C2—H2A	109.8	C11—C10—H10B	109.7
C1—C2—H2B	109.8	C14—C10—H10B	109.7
C7—C2—H2B	109.8	H10A—C10—H10B	108.2
H2A—C2—H2B	108.3	N4—C11—C10	109.8 (2)
N1—C3—C4	109.5 (2)	N4—C11—H11A	109.7
N1—C3—H3A	109.8	C10—C11—H11A	109.7
C4—C3—H3A	109.8	N4—C11—H11B	109.7
N1—C3—H3B	109.8	C10—C11—H11B	109.7
C4—C3—H3B	109.8	H11A—C11—H11B	108.2
H3A—C3—H3B	108.2	N3—C12—C14	122.8 (2)
C3—C4—C7	109.9 (2)	N3—C12—C13	124.3 (2)

C3—C4—H4A	109.7	C14—C12—C13	112.83 (19)
C7—C4—H4A	109.7	N4—C13—C12	108.2 (2)
C3—C4—H4B	109.7	N4—C13—H13A	110.1
C7—C4—H4B	109.7	C12—C13—H13A	110.1
H4A—C4—H4B	108.2	N4—C13—H13B	110.1
N1—C5—C6	108.1 (2)	C12—C13—H13B	110.1
N1—C5—H5A	110.1	H13A—C13—H13B	108.4
C6—C5—H5A	110.1	C12—C14—C8	106.5 (2)
N1—C5—H5B	110.1	C12—C14—C10	107.9 (2)
C6—C5—H5B	110.1	C8—C14—C10	108.7 (2)
H5A—C5—H5B	108.4	C12—C14—H14A	111.2
N2—C6—C5	124.7 (2)	C8—C14—H14A	111.2
N2—C6—C7	122.5 (2)	C10—C14—H14A	111.2
C5—C6—C7	112.7 (2)	C5—N1—C1	110.5 (2)
C6—C7—C4	106.5 (2)	C5—N1—C3	109.6 (2)
C6—C7—C2	107.8 (2)	C1—N1—C3	109.8 (2)
C4—C7—C2	109.6 (2)	C5—N1—H1C	109.0
C6—C7—H7A	110.9	C1—N1—H1C	109.0
C4—C7—H7A	110.9	C3—N1—H1C	109.0
C2—C7—H7A	110.9	C13—N4—C9	109.8 (2)
C9—C8—C14	109.8 (2)	C13—N4—C11	110.5 (2)
C9—C8—H8A	109.7	C9—N4—C11	109.4 (2)
C14—C8—H8A	109.7	C13—N4—H4C	109.0
C9—C8—H8B	109.7	C9—N4—H4C	109.0
C14—C8—H8B	109.7	C11—N4—H4C	109.0
H8A—C8—H8B	108.2	C6—N2—N3	111.9 (2)
N4—C9—C8	110.1 (2)	C12—N3—N2	112.7 (2)