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Crystal structure of 2,2-diphenylhydrazinium chloride

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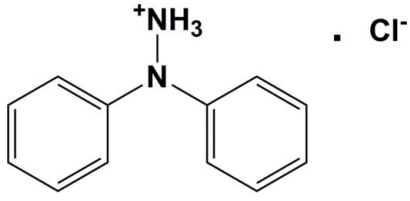
In the title compound, $C_{12}H_{13}N_2^+\cdot Cl^-$, the chloride salt of 1,1′-diphenylhydrazine, the phenyl rings are inclined to one another by 78.63 (17)°. The N—$^+NH_3$ bond lengths is 1.445 (3) Å, and the N—C_{phenyl} bond lengths are 1.435 (3) and 1.447 (4) Å. In the crystal, molecules are linked *via* N—H···Cl hydrogen bonds, forming chains along [10$\bar{1}$], which enclose two adjacent $R_2^4(6)$ ring motifs. The chains are reinforced by C—H···Cl hydrogen bonds.

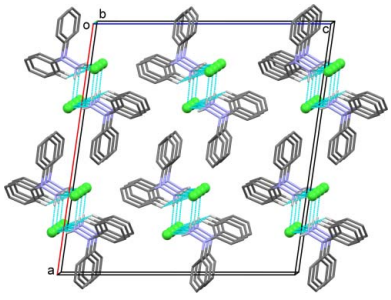
1. Chemical context

1,1′-Diphenylhydrazine is a 'free' hydrazine, *viz* with an NH_2 group. It has been used as a starting reagent for the preparation of Schiff bases as fluorescent sensors for fluoride (Mukherjee *et al.*, 2014), and metal complexes (Stender *et al.*, 2003; Clulow *et al.*, 2008). The title compound, (I), crystallized out of a reaction of 1,1′-diphenylhydrazine with 2,6-diacetylpyridine in an attempt to prepare the ligand 2,6-diacetylpyridine bis(*N*,*N*-diphenylhydrazone). The latter compound is one of a series that has been used to prepare bis(imino)pyridyl iron and cobalt complexes to study the effect of nitrogen substituents on ethylene oligomerization and polymerization (Britovsek *et al.*, 2001).



2. Structural commentary

The molecular structure of the title salt, (I), is illustrated in Fig. 1, and selected bond distances and bond angles are given



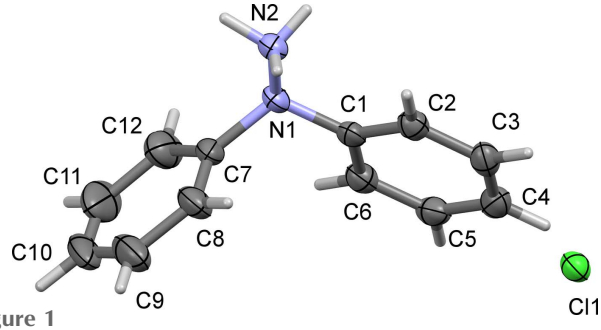


Figure 1
A view of the molecular structure of the title compound with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.445 (3)	N1—C7	1.447 (4)
N1—C1	1.435 (3)		
C1—N1—N2	113.4 (2)	N2—N1—C7	111.5 (2)
C1—N1—C7	116.0 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1*N*···Cl1^{i}	0.92 (3)	2.31 (3)	3.208 (3)	165 (3)
N2—H2*N*···Cl1^{ii}	0.96 (3)	2.23 (3)	3.167 (3)	167 (3)
N2—H3*N*···Cl1^{iii}	0.86 (4)	2.30 (4)	3.154 (3)	175 (3)
C2—H2···Cl1^{i}	0.95	2.96	3.696 (3)	135

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

in Table 1. The two phenyl rings (C1–C6 and C7–C12) are inclined to one another by 78.63 (17)°. The N1—N2 bond lengths is 1.445 (3) Å and the N1—C1 and N1—C7 bond lengths are 1.435 (3) and 1.447 (4) Å, respectively. Atom N1 is displaced from the plane of the three connected atoms, (N2/C1/C7), by 0.370 (2) Å, while the sum of the three angles involving atom N1 is 340.9 °. This illustrates clearly the pyramidal nature of the central N atom, N1.

3. Supramolecular features

In the crystal of compound (I), molecules are linked *via* N—H···Cl hydrogen bonds, forming chains along [10$\bar{1}$], which enclose two adjacent $R_2^4(6)$ ring motifs (Table 2 and Fig. 2). The chains are reinforced by C—H···Cl hydrogen bonds (Fig. 3 and Table 2).

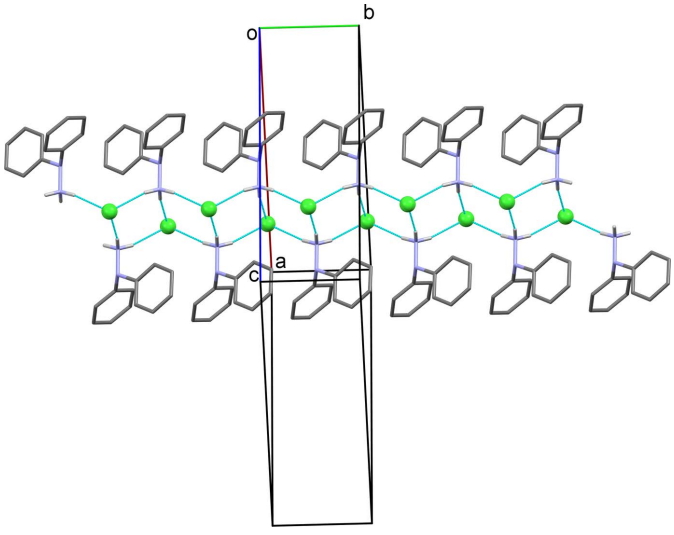


Figure 2
A partial view normal to (10$\bar{1}$) of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines (see Table 2 for details; C-bound H atoms have been omitted for clarity).

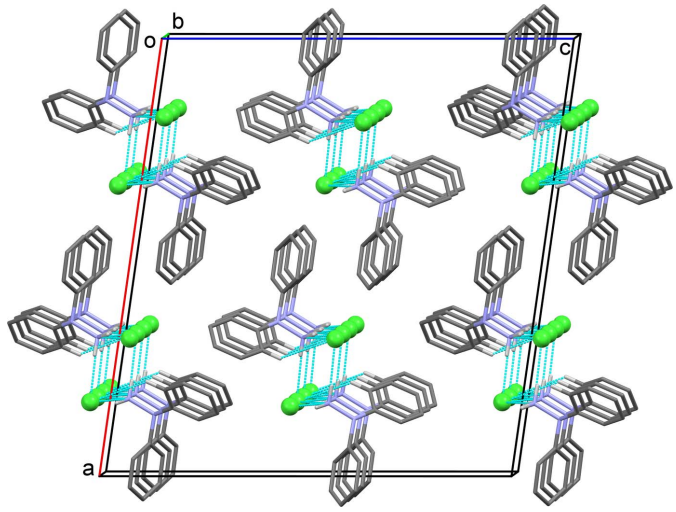


Figure 3
A view along the *b* axis of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines (see Table 2 for details; C-bound H atoms not involved in hydrogen bonding have been omitted for clarity).

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update May 2014; Groom & Allen, 2014) yielded only two hits for the sub-structure 1,1′-diphenylhydrazine: *viz*. 1,1′-diphenylhydrazinium dicyanogold(I) monohydrate (II) (Stender *et al.*, 2003) and 1,1′-diphenylhydrazine (III) itself (Clulow *et al.*, 2008).

The structure of salt (II) is very similar to that of the title compound, (I). The two phenyl rings are inclined to one another by 80.04 (19)° compared to 78.63 (17)° in (I). The bond lengths and angles involving the central N atom are also very similar to those in (I). The central N atom is displaced by 0.358 (3) Å from the plane of the three attached N and C atoms, and the sum of their bond angles is 342.0°, indicating clearly the pyramidal nature of the central N atom, as in (I).

In 1,1′-diphenylhydrazine (III), which crystallized with two independent molecules per asymmetric unit, the phenyl rings are inclined to one another by only 58.39 (2) and 52.30 (9)°, and the N—NH_2 bond lengths are 1.418 (2) and 1.411 (3) Å. The central N atoms are displaced by 0.1199 (17) and 0.0828 (19) Å from the planes of the three attached N and C atoms, with the sums of their bond angles being 357.85 and 358.97°. This confirms the trigonal–planar conformation of the central N atom.

In the crystal of compound (II), molecules are linked by N—H···N, N—H···O and O—H···N hydrogen bonds, forming two-dimensional networks parallel to (001). These sheets are linked *via* C—H···π interactions, forming a three-dimensional structure. In the crystal of compound (III), there are no hydrogen bonds present with only weak C—H···π interactions linking the molecules to form chains along [100]. There are no π–π interactions present in the crystal structures of any of the three compounds.

5. Synthesis and crystallization

Brown block-like crystals of the title compound were obtained during an attempt to prepare the ligand 2,6-diacetylpyridine bis(*N*,*N*-diphenylhydrazone) by a condensation reaction involving 1,1′-diphenylhydrazinium hydrochloride and 2,6-diacetylpyridine in methanol.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. The ammonium H atoms were located in a difference Fourier map and freely refined. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å with U_{iso}(H) = 1.2U_{eq}(C).

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{13}N_2^+\cdot Cl^-$
M_r	220.69
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	173
a, *b*, *c* (Å)	21.341 (3), 5.3728 (4), 19.940 (3)
β (°)	98.291 (10)
V (Å^3)	2262.4 (5)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.31
Crystal size (mm)	0.45 × 0.35 × 0.25
Data collection	
Diffractometer	STOE IPDS 2
Absorption correction	Multi-scan (*MULscanABS* in *PLATON*; Spek, 2009)
T_{min}, T_{max}	0.578, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7392, 2140, 1517
R_{int}	0.120
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.057, 0.141, 0.93
No. of reflections	2140
No. of parameters	148
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.47

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2009), *SHELXS2013* and *SHELXL2013* (Sheldrick, 2008), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008), and *publCIF* (Westrip, 2010).

Acknowledgements

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

2,2-Diphenylhydrazinium chloride

Crystal data

$C_{12}H_{13}N_2^+\cdot Cl^-$
M_r = 220.69
Monoclinic, $C2/c$
a = 21.341 (3) Å
b = 5.3728 (4) Å
c = 19.940 (3) Å
β = 98.291 (10)°
V = 2262.4 (5) Å^3
Z = 8
$F(000)$ = 928
D_x = 1.296 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5046 reflections
θ = 1.9–26.0°
μ = 0.31 mm^{-1}
T = 173 K
Block, brown
0.45 × 0.35 × 0.25 mm

Data collection

STOE IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
$\varphi + \omega$ scans
Absorption correction: multi-scan (*MULscanABS* in *PLATON*; Spek, 2009)
T_{min} = 0.578, T_{max} = 1.000
7392 measured reflections
2140 independent reflections
1517 reflections with $I > 2\sigma(I)$
R_{int} = 0.120
θ_{max} = 25.6°, θ_{min} = 1.9°
h = −24→25
k = −6→5
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.141
S = 0.93
2140 reflections
148 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0794P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.14173 (10)	0.9765 (4)	0.38714 (11)	0.0284 (5)
N2	0.17735 (12)	0.9687 (5)	0.45449 (12)	0.0296 (5)
H1N	0.1692 (14)	0.834 (6)	0.4807 (14)	0.032 (8)*
H2N	0.1695 (15)	1.113 (6)	0.4803 (14)	0.034 (8)*
H3N	0.217 (2)	0.982 (7)	0.4537 (17)	0.046 (10)*
C1	0.15920 (13)	0.7846 (5)	0.34332 (13)	0.0282 (6)
C2	0.20210 (14)	0.5967 (5)	0.36467 (14)	0.0312 (6)
H2	0.2207	0.5880	0.4108	0.037*
C3	0.21793 (14)	0.4209 (5)	0.31865 (14)	0.0345 (7)
H3	0.2470	0.2917	0.3336	0.041*
C4	0.19146 (15)	0.4339 (6)	0.25115 (15)	0.0376 (7)
H4	0.2025	0.3151	0.2196	0.045*
C5	0.14855 (14)	0.6226 (6)	0.23008 (14)	0.0357 (7)
H5	0.1301	0.6317	0.1838	0.043*
C6	0.13236 (14)	0.7966 (5)	0.27525 (14)	0.0336 (6)
H6	0.1030	0.9246	0.2601	0.040*
C7	0.07462 (14)	1.0052 (5)	0.38918 (15)	0.0334 (7)
C8	0.04095 (15)	0.8348 (7)	0.42154 (16)	0.0438 (8)
H8	0.0617	0.6955	0.4442	0.053*
C9	−0.02370 (18)	0.8694 (9)	0.42060 (19)	0.0622 (11)
H9	−0.0474	0.7536	0.4427	0.075*
C10	−0.05343 (18)	1.0729 (10)	0.3874 (2)	0.0708 (14)
H10	−0.0976	1.0975	0.3870	0.085*
C11	−0.0194 (2)	1.2384 (9)	0.3551 (3)	0.0798 (15)
H11	−0.0405	1.3756	0.3317	0.096*
C12	0.04547 (17)	1.2096 (7)	0.3560 (2)	0.0561 (10)
H12	0.0691	1.3272	0.3344	0.067*
Cl1	0.17516 (3)	0.53583 (13)	0.04013 (3)	0.0316 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0175 (11)	0.0303 (12)	0.0360 (12)	0.0013 (9)	−0.0004 (9)	−0.0032 (9)
N2	0.0203 (13)	0.0317 (13)	0.0361 (13)	−0.0011 (11)	0.0012 (10)	−0.0047 (11)
C1	0.0192 (14)	0.0282 (14)	0.0376 (14)	−0.0040 (11)	0.0052 (11)	−0.0018 (11)
C2	0.0271 (15)	0.0305 (15)	0.0363 (14)	−0.0017 (12)	0.0055 (12)	0.0028 (11)
C3	0.0308 (17)	0.0290 (15)	0.0460 (16)	0.0025 (12)	0.0128 (13)	0.0030 (12)
C4	0.0348 (18)	0.0366 (16)	0.0441 (16)	−0.0056 (14)	0.0148 (13)	−0.0082 (13)
C5	0.0291 (16)	0.0414 (16)	0.0363 (15)	−0.0084 (13)	0.0039 (12)	−0.0036 (12)

C6	0.0255 (15)	0.0348 (15)	0.0401 (15)	−0.0010 (12)	0.0036 (12)	0.0034 (12)
C7	0.0203 (14)	0.0348 (16)	0.0433 (15)	0.0017 (12)	−0.0013 (11)	−0.0123 (12)
C8	0.0226 (16)	0.057 (2)	0.0510 (18)	−0.0017 (15)	0.0043 (13)	−0.0060 (15)
C9	0.031 (2)	0.096 (3)	0.062 (2)	−0.008 (2)	0.0132 (17)	−0.025 (2)
C10	0.0222 (19)	0.102 (4)	0.084 (3)	0.008 (2)	−0.0050 (18)	−0.050 (3)
C11	0.041 (2)	0.067 (3)	0.120 (4)	0.024 (2)	−0.026 (2)	−0.027 (3)
C12	0.036 (2)	0.045 (2)	0.082 (3)	0.0090 (16)	−0.0091 (17)	−0.0038 (18)
Cl1	0.0232 (4)	0.0334 (4)	0.0381 (4)	0.0010 (3)	0.0044 (3)	0.0008 (3)

Geometric parameters (Å, º)

N1—N2	1.445 (3)	C5—C6	1.376 (4)
N1—C1	1.435 (3)	C5—H5	0.9500
N1—C7	1.447 (4)	C6—H6	0.9500
N2—H1N	0.92 (3)	C7—C8	1.380 (5)
N2—H2N	0.96 (3)	C7—C12	1.383 (4)
N2—H3N	0.86 (4)	C8—C9	1.390 (5)
C1—C2	1.388 (4)	C8—H8	0.9500
C1—C6	1.397 (4)	C9—C10	1.384 (7)
C2—C3	1.392 (4)	C9—H9	0.9500
C2—H2	0.9500	C10—C11	1.365 (7)
C3—C4	1.384 (4)	C10—H10	0.9500
C3—H3	0.9500	C11—C12	1.392 (6)
C4—C5	1.390 (4)	C11—H11	0.9500
C4—H4	0.9500	C12—H12	0.9500
C1—N1—N2	113.4 (2)	C4—C5—H5	119.5
C1—N1—C7	116.0 (2)	C5—C6—C1	119.9 (3)
N2—N1—C7	111.5 (2)	C5—C6—H6	120.1
N1—N2—H1N	115.5 (19)	C1—C6—H6	120.1
N1—N2—H2N	111.5 (18)	C8—C7—C12	121.5 (3)
H1N—N2—H2N	106 (3)	C8—C7—N1	121.8 (3)
N1—N2—H3N	112 (2)	C12—C7—N1	116.8 (3)
H1N—N2—H3N	110 (3)	C7—C8—C9	119.2 (4)
H2N—N2—H3N	101 (3)	C7—C8—H8	120.4
C2—C1—C6	119.5 (3)	C9—C8—H8	120.4
C2—C1—N1	123.6 (2)	C10—C9—C8	119.9 (4)
C6—C1—N1	116.9 (2)	C10—C9—H9	120.1
C1—C2—C3	120.2 (3)	C8—C9—H9	120.1
C1—C2—H2	119.9	C11—C10—C9	120.1 (4)
C3—C2—H2	119.9	C11—C10—H10	119.9
C4—C3—C2	120.2 (3)	C9—C10—H10	119.9
C4—C3—H3	119.9	C10—C11—C12	121.2 (4)
C2—C3—H3	119.9	C10—C11—H11	119.4
C3—C4—C5	119.3 (3)	C12—C11—H11	119.4
C3—C4—H4	120.4	C7—C12—C11	118.2 (4)
C5—C4—H4	120.4	C7—C12—H12	120.9
C6—C5—C4	120.9 (3)	C11—C12—H12	120.9

C6—C5—H5	119.5		
N2—N1—C1—C2	5.2 (4)	C1—N1—C7—C8	72.9 (3)
C7—N1—C1—C2	−125.8 (3)	N2—N1—C7—C8	−59.0 (3)
N2—N1—C1—C6	−172.7 (2)	C1—N1—C7—C12	−105.9 (3)
C7—N1—C1—C6	56.3 (3)	N2—N1—C7—C12	122.2 (3)
C6—C1—C2—C3	−0.4 (4)	C12—C7—C8—C9	0.1 (5)
N1—C1—C2—C3	−178.2 (2)	N1—C7—C8—C9	−178.7 (3)
C1—C2—C3—C4	0.7 (4)	C7—C8—C9—C10	0.1 (5)
C2—C3—C4—C5	−0.6 (4)	C8—C9—C10—C11	0.5 (6)
C3—C4—C5—C6	0.3 (4)	C9—C10—C11—C12	−1.3 (6)
C4—C5—C6—C1	0.0 (4)	C8—C7—C12—C11	−0.8 (5)
C2—C1—C6—C5	0.1 (4)	N1—C7—C12—C11	178.0 (3)
N1—C1—C6—C5	178.1 (2)	C10—C11—C12—C7	1.4 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*···Cl1^{i}	0.92 (3)	2.31 (3)	3.208 (3)	165 (3)
N2—H2*N*···Cl1^{ii}	0.96 (3)	2.23 (3)	3.167 (3)	167 (3)
N2—H3*N*···Cl1^{iii}	0.86 (4)	2.30 (4)	3.154 (3)	175 (3)
C2—H2···Cl1^{i}	0.95	2.96	3.696 (3)	135

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