Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of 3,6,6-trimethyl-4-oxo-1-(pyridin-2-yl)-4,5,6,7-tetrahydro-1*H*-indazol-7-aminium chloride and its monohydrate

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Received 26 September 2017
Accepted 20 November 2017

Edited by E. V. Boldyreva, Russian Academy of Sciences, Russia

Keywords: crystal structure; tetrahydroindazole; tetrahydroindazolone; hydrochloride; hydrate.

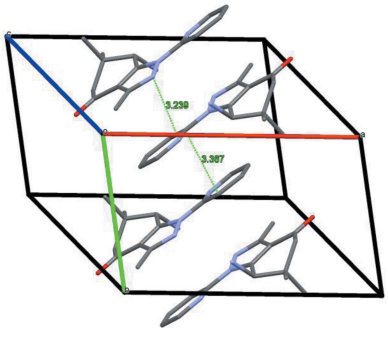
CCDC references: 1586488; 1586487

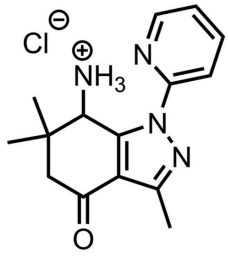
Supporting information: this article has supporting information at journals.iucr.org/e

The title compounds, $C_{15}H_{19}N_4O^+\cdot Cl^-$ and $C_{15}H_{19}N_4O^+\cdot Cl^-\cdot H_2O$, obtained in attempts to synthesize metal complexes using tetrahydroindazole as a ligand, were characterized by NMR, IR and X-ray diffraction techniques. The partially saturated ring in the tetrahydroindazole core adopts a sofa conformation. An intramolecular N—H···N hydrogen bond formed by the protonated amino group and the N atom of the pyridyl substituent is found in the first structure. In the hydrochloride, the organic moieties are linked by two N—H···Cl^- hydrogen bonds, forming a $C(4)$ graph-set. In the hydrate crystal, a Cl^- anion and a water molecule assemble the moieties into infinite bands showing hydrogen-bond patterns with graph sets $C(6)$, $R_6^4(12)$ and $R_4^2(8)$. Organic moieties form π–π stacked supramolecular structures running along the *b* axis in both structures.

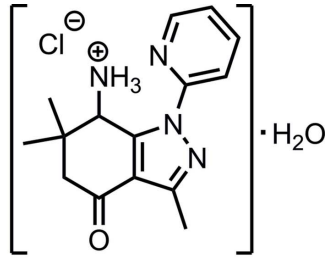
1. Chemical context

Tetrahydroindazoles can be regarded as annulated pyrazole analogs (Ansari *et al.*, 2017) or as partially saturated indazoles (Gaikwad *et al.*, 2015). In either of these categories they play an important role in medicinal chemistry. Tetrahydroindazoles are reported to be peripherally selective cannabinoid-1 receptor inverse agonists (Matthews *et al.*, 2016), sigma-2 receptor ligands(Wu *et al.*, 2015), and interleukin-2 inducible T-cell kinase inhibitors (Burch *et al.*, 2015; Heifetz *et al.*, 2016). Heterocyclic compounds containing a tetrahydroindazole core have been researched as antiviral agents (Bassyouni *et al.*, 2016) and compounds with antioxidant properties (Polo *et al.*, 2016). With appropriate side-chain decorations, they also possess COX-2 inhibitory activity (Abdel-Rahman *et al.*, 2012) and can inhibit bacterial type II topoisomerases (Wiener *et al.*, 2007). The latter has led to the development of compounds with both antitumor and antimicrobial activity (Faidallah *et al.*, 2013), including novel antituberculosis agents (Guo *et al.*, 2010).





1



2

The broad application spectrum of tetrahydroindazoles has led to the development of synthetic methodologies. Thus, traditional approaches using a combination of either α,β-unsaturated ketones (Nakhai & Bergman, 2009) or dicarbonyl compounds (Murugavel *et al.*, 2010), or tricarbonyl compounds (Kim *et al.*, 2010; Scala *et al.*, 2015) with hydrazines have been significantly updated and improved. In addition, the microwave-assisted synthesis of tetrahydroindazoles has been reported (Silva *et al.*, 2006; Polo *et al.*, 2016). It is interesting to note that compounds possessing free NH-functionality in the pyrazole ring have been studied thoroughly for their tautomeric equilibria (Claramunt *et al.*, 2006). Additionally, tetrahydroindazolones substituted with 2-aminobenzamides have been studied as fluorescent probes (Jia *et al.*, 2012). Other studies on side-chain modifications include the synthesis of polyfluoroalkyl-substituted analogs (Khlebnikova *et al.*, 2012), triazole-functionalized tetrahydroindazolones (Strakova *et al.*, 2009) and their conjugation with biologically active natural products such as lupane triterpenoids (Khlebnicova *et al.*, 2017). Among other synthetic approaches, the Ritter reaction provides a fast entry into structural modifications and is applicable to obtain a combinatorial library of compounds (Turks *et al.*, 2012). Combinatorial chemistry methodology has been reported for the construction of tetrahydroindazolones in enantiomerically pure pairs (Song *et al.*, 2012). Also, enantiomerically pure 7-amino-tetrahydroindazolones (Strakova *et al.*, 2011) have been obtained. For these reasons, we were interested in the synthesis of 7-amino-3,6,6-trimethyl-1-(pyridin-2-yl)-1,5,6,7-tetrahydro-4*H*-indazol-4-one for use as a starting material for further structural modifications. Herein, the structures of the corresponding hydrochloride **1** and its hydrate **2** are reported.

2. Structural commentary

Figs. 1 and 2 show the asymmetric units of the hydrochloride (**1**) and its hydrate (**2**) with the symmetry-independent hydrogen bonds. The geometry and conformation of the organic cation in compounds **1** and **2** are substantially similar. The pyrazole ring is planar within an r.m.s. deviation of the fitted atoms of 0.0059 Å in **1** and 0.0092 Å in **2**. In both structures, the partially saturated ring adopts a sofa conformation. The distance of atom C6 from the mean plane formed by atoms C3–C5/C7/C8 (r.m.s. deviation of fitted atoms = 0.0495 Å in **1** and 0.0558 Å in **2**) is 0.639 (2) Å in **1** and 0.642 (2) Å in **2**. The dihedral angle between the latter plane and pyrazole ring is 5.79 (6)° in **1** and 6.48 (4)° in **2**. On the other hand, the dihedral angle between the pyrazole ring and its pyridyl substituent is 11.91 (6)° [torsion angle N4—N3—C11—C12 = 10.7 (2)°] in **1** and 7.22 (5)° [torsion angle N4—N3—C11—C12 = 4.6 (2)°] in **2**. An intramolecular N—H···N hydrogen bond formed by the protonated amino group and nitrogen atom of pyridyl substituent is found in **1** (Table 1).

3. Supramolecular features

In the crystal of compound **1**, the organic moieties are linked by two types of N—H···Cl$^-$ hydrogen bonds into infinite chains along the *b*-axis direction (Table 1). According to Etter (1990), the hydrogen-bond pattern in **1** can be described by a

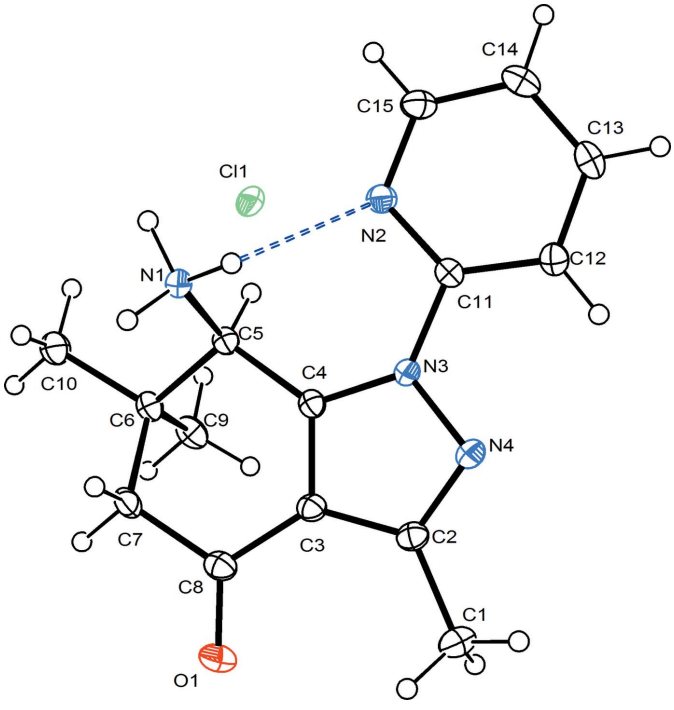


Figure 1
ORTEP view of the asymmetric unit of **1** showing the atom-numbering scheme and 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown with dashed lines.

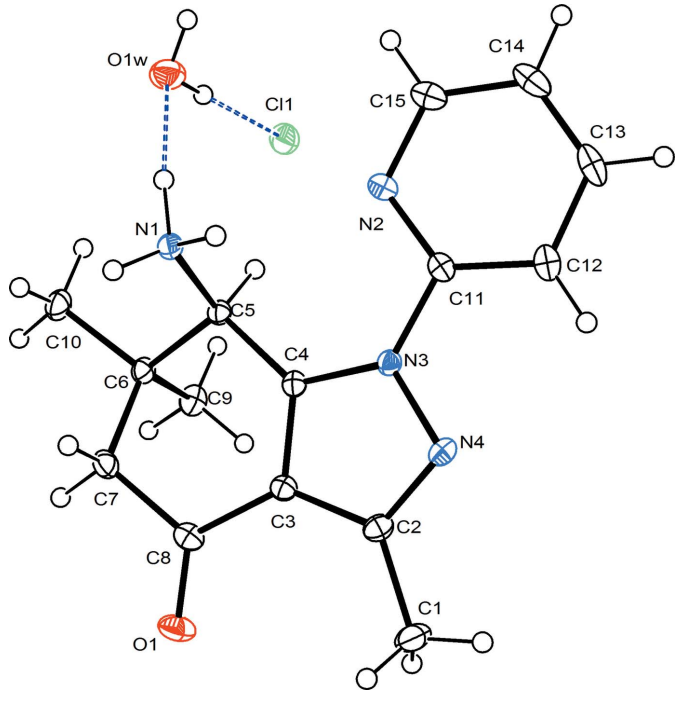


Figure 2
ORTEP view of the asymmetric unit of **2** showing the atom-numbering scheme and 50% probability displacement ellipsoids. The intramolecular hydrogen bonds are shown with dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*1···N2	0.97 (2)	2.42 (2)	2.928 (2)	112 (2)
N1—H2*N*1···Cl1^{i}	0.97 (2)	2.08 (2)	3.034 (2)	168 (2)
N1—H3*N*1···Cl1^{ii}	0.93 (2)	2.27 (2)	3.188 (2)	167 (2)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*W*···Cl1^{i}	0.80 (3)	2.39 (3)	3.185 (2)	176 (3)
O1*W*—H2*W*···Cl1	0.94 (3)	2.31 (3)	3.247 (2)	179 (2)
N1—H1*N*1···Cl1^{ii}	0.85 (2)	2.40 (2)	3.228 (2)	165 (2)
N1—H3*N*1···O1*W*	0.95 (2)	1.85 (3)	2.775 (2)	162 (2)

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

$C(4)$ graph set. The packing of **1** is shown in Fig. 3. In the structure of **2**, in addition to participating in an intramolecular hydrogen bond, the protonated amino group also forms two intermolecular hydrogen bonds with the Cl^- anion and a water molecule (Table 2). Each Cl^- anion and water molecule takes part in three intermolecular hydrogen bonds. The organic cations are bridged by a pair of Cl^- anions and a water molecule, thus assembling the moieties into infinite bands running along the *b*-axis direction. The hydrogen-bond pattern can be described by graph sets $C(6)$, $R_6^4(12)$ and $R_4^2(8)$. The packing of **2** is shown in Fig. 4.

In the crystal of **1**, the organic moieties form stacks running along the *b* axis which are stabilized by π–π interactions (Fig. 5). The distance between the centroids of the pyridine and pyrazole rings of adjacent molecules is 3.585 (2) Å. The shortest contact is 3.239 (2) Å between atoms N2 and N4 of two inversion-related molecules (Fig. 5). In the crystal of **2**, the organic moieties also form π–π-stacked supramolecular

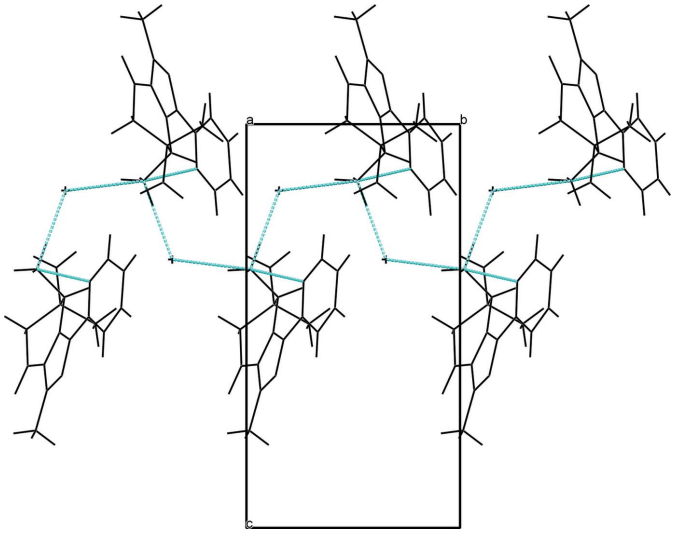


Figure 3
The crystal packing of compound **1**, viewed along the *a* axis. The hydrogen bonds are shown as dashed lines (see Table 1).

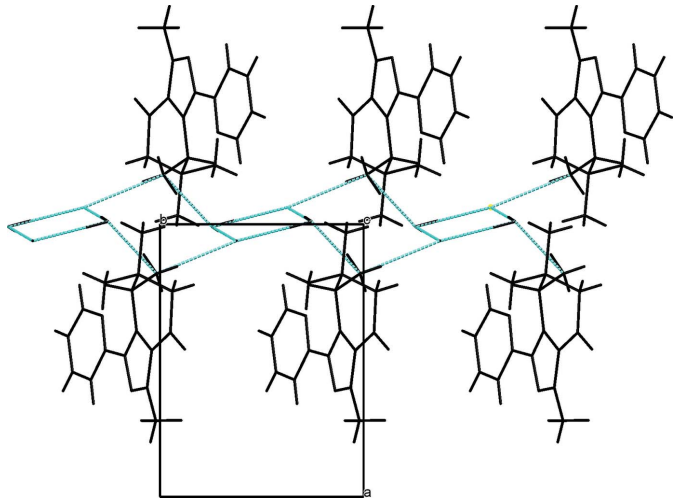


Figure 4
The crystal packing of compound **2**, viewed along the *c* axis. The hydrogen bonds are shown as dashed lines (see Table 2).

structures running along the *b*-axis direction (Fig. 6). The distance between the centroids of the pyridine rings of adjacent molecules is 3.748 (2) Å. The shortest contact is 3.170 (2) Å between the N3 atoms of two inversion-related molecules (Fig. 6).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38; Groom *et al.*, 2016) for the 3,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydro-1*H*-indazole core revealed five structurally close compounds: UXAQUG, UXARAN, UXARER, UXARIV, UXAROB (Strakova *et al.*, 2011). These compounds differ from compounds **1** and **2** by the substituents at the positions of atoms N3 and C5. In all examples, the partially saturated ring in the indazole fragment adopts a sofa conformation.

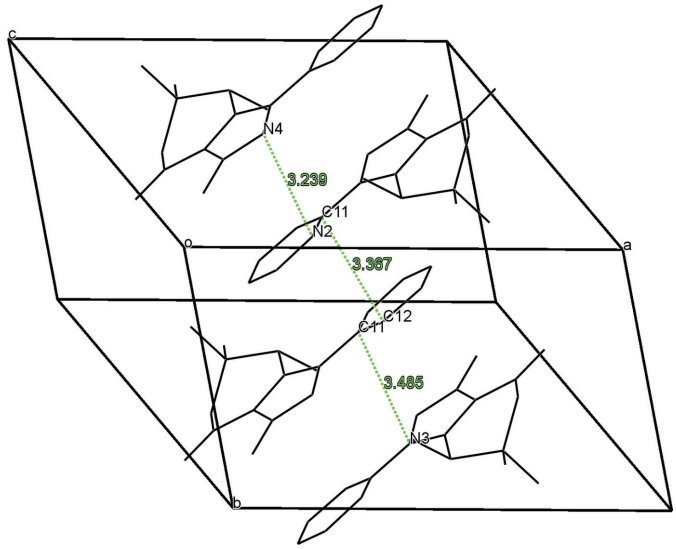


Figure 5
View of stacks of organic moieties in the crystal structure of **1**. H atoms and chloride anions are not shown for clarity.

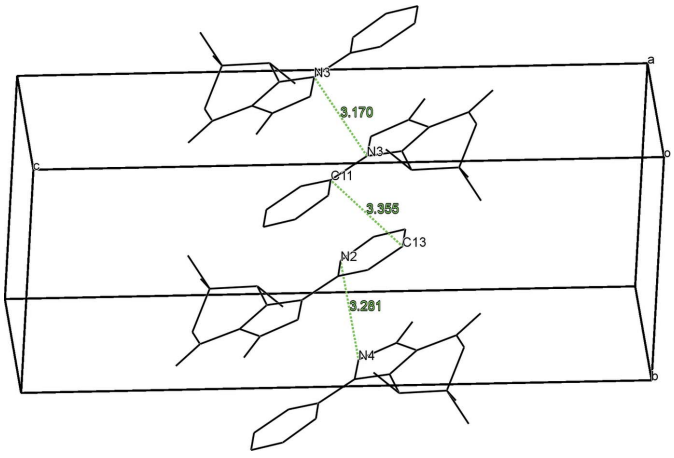
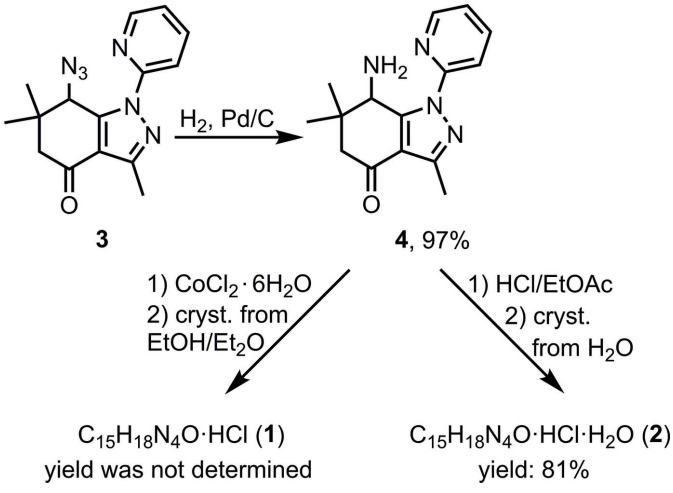


Figure 6
View of stacks of organic moieties in the crystal structure of **2**. H atoms, chloride anions and water molecules are not shown for clarity.

However, the phenyl ring at the position N3 forms much larger dihedral angles with the pyrazole ring than with the pyridyl substituent in the structures reported here.

5. Synthesis and crystallization

The synthesis of the title compounds is depicted in the reaction scheme below. The 7-aminotetrahydroindazolone derivative **4** was prepared by an analogy of the procedure published by Strakova *et al.* (2011) from the known precursor **3** (Strakova *et al.*, 2009). In our attempts to synthesize metal complexes with ligand **4**, we obtained the hydrochloride salt **1** in its anhydrous form. It can be explained by the acidity of cobalt chloride hexahydrate, which was used in the selected experiment. This prompted us to develop a preparative synthesis of the hydrochloride salt. This was achieved by the formation and precipitation of crude hydrochloride in ethyl acetate solution. Its crystallization from water provided the hydrochloride hydrate **2**.



7-Amino-3,6,6-trimethyl-1-(pyridin-2-yl)-1,5,6,7-tetrahydro-4*H*-indazol-4-one (4): Gaseous H_2 was bubbled for 10 min. through a solution/suspension of compound **3** (0.80 g, 2.7 mmol) and 10% Pd/C (80 mg) in a mixture of EtOH (10 mL) and THF (2 mL). The resulting reaction mixture was stirred under an H_2 atmosphere at standard temperature and pressure for 3 h (TLC control). The catalyst was filtered through a celite pad and the filtrate was evaporated to dryness. The resulting amorphous solid was dried under reduced pressure to yield amine **4** (0.71 g, 97%) as a colorless powder. M.p. 390–392 K; R_f = 0.14 (Hex:EtOAc:Et_3N = 8:1:0.5). IR (KBr), υ (cm^{-1}): 3360, 3295, 3055, 2985, 2955, 2945, 2930, 2890, 2865, 1670, 1590, 1575, 1540, 1465, 1455, 1285, 1250, 1145, 1085, 1075, 1035, 995. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.48 [*m*, 1H, H-C(Py)], 7.99 [*d*, *J* = 8.3 Hz, 1H, H-C(Py)], 7.87 [*m*, 1H, H-C(Py)], 7.26 [*m*, 1H, H-C(Py)], 4.27 (*s*, 1H, H-C7), 2.82 (*d*, *J* = 16.8 Hz, 1H, H_a-C5), 2.54 (*s*, 3H, H_3C-C3), 2.18 (*d*, *J* = 16.8 Hz, 1H, H_b-C5), 2.08 (*bs*, 2H, H_2N-C7) 1.26, 1.02 (2*s*, 6H, H_3C-C6).^{13}C NMR (75.5 MHz, $CDCl_3$), δ (ppm): 194.1, 153.9, 152.4, 150.4, 148.0, 139.1, 122.1, 116.5, 115.9, 53.8, 47.8, 38.4, 27.3, 26.6, 13.7. Analysis calculated: ($C_{15}H_{18}N_4O$) C, 66.64; H, 6.71; N, 20.73. Found: C, 66.56; H, 6.68; N, 20.74.

3,6,6-Trimethyl-4-oxo-1-(pyridin-2-yl)-4,5,6,7-tetrahydro-1*H*-indazol-7-aminium chloride (1): A solution of $CoCl_2·6H_2O$ (24 mg, 0.1 mmol) in ethanol (2 mL) was added to a solution of amine **4** (27 mg, 0.1 mmol) in ethanol (2 mL). The resulting reaction mixture was maturated at ambient temperature for 24 h. Then a part of it (1.2 mL) was transferred into an NMR tube and Et_2O (0.8 mL) was added carefully on the top of the ethanol solution. After two days, colorless crystals of **1** were collected form the wall of the NMR tube. The product was characterized spectroscopically in its hydrate form (see below).

3,6,6-Trimethyl-4-oxo-1-(pyridin-2-yl)-4,5,6,7-tetrahydro-1*H*-indazol-7-aminium chloride hydrate (2): A solution of HCl in EtOAc (0.5 *M*, 1.48 mL, 0.74 mmol, 1.0 equiv.) was added to a solution of amine **4** (0.20 g, 0.74 mmol, 1.0 equiv.) in EtOAc (2 mL) at ambient temperature. The resulting precipitate was filtered and washed on the filter with DCM. The the crude product was crystallized from water to obtain colorless crystals of **2** (195 mg, 81%) suitable for X-ray analysis. M.p. 543 K (decomp.); IR (KBr), υ (cm^{-1}): 3430 (*br.s*), 3145, 3100, 3035, 2965, 2880, 2750, 2575, 1955 (*br.s*), 1685, 1600, 1545, 1520, 1490, 1465, 1450, 1400, 1375, 1360, 1295, 1245, 1140, 1045, 1000, 955. ^{1}H NMR (300MHz, D_2O), δ (ppm): δ 8.55 [*m*, 1H, H-C(Py)], 8.12 [*m*,1H,H-C (Py)], 7.90 [*d*, *J* = 8.3 Hz, 1H, H-C(Py)], 7.53 [*m*, 1H, H-C(Py)], 4.84 (*s*, 1H, H-C7), 3.00 (*d*, *J* =17.8 Hz, 1H, H_a-C5), 2.54 (*s*, 3H, H_3C-C3), 2.45 (*d*, *J* = 17.8Hz,1H,H_b-C5), 1.36, 1.10 (2*s*, 6H, H_3C-C6). ^{13}C NMR (75.5 MHz, DMSO-d_6), δ (ppm):192.3, 151.4, 149.0, 148.0, 144.4, 140.1, 122.8, 118.0, 114.6, 51.4, 47.1, 37.2, 26.8, 25.4, 13.2. Analysis calculated: ($C_{15}H_{18}N_4O·HCl·H_2O$) C, 55.47; H, 6.52; N, 17.25. Found: C, 55.78; H,6.40; N, 17.29.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms bonded to heteroatoms were refined isotropically. Other H atoms were included in the refinement at geometrically calculated posi-

Table 3
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$C_{15}H_{19}N_4O^+\cdot Cl^-$	$C_{15}H_{19}N_4O^+\cdot Cl^-\cdot H_2O$
M_r	306.79	324.81
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	190	190
a, b, c (Å)	13.5411 (4), 7.7421 (2), 19.2457 (5)	10.1855 (2), 7.4951 (2), 20.7961 (4)
β (°)	130.493 (2)	100.545 (1)
V (Å^3)	1534.39 (8)	1560.79 (6)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.25	0.26
Crystal size (mm)	0.38 × 0.32 × 0.15	0.42 × 0.25 × 0.14
Data collection		
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5860, 3486, 2715	5549, 3552, 2874
R_{int}	0.027	0.023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.654
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.101, 1.03	0.039, 0.102, 1.06
No. of reflections	3486	3552
No. of parameters	205	222
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.25	0.29, −0.28

Computer programs: *COLLECT* (Bruker, 2004), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO* (Otwinowski & Minor, 1997), *SIR2004* (Burla *et al.*, 2005), *SHELXL2017* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

tions with C—H = 0.95–0.99Å and treated as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C-methyl).

Funding information

Funding for this research was provided by: Latvian Council of Science (grant No. 14.0593).

References

Abdel-Rahman, H. M. & Ozadali, K. (2012). *Arch. Pharm. Pharm. Med. Chem.* **345**, 878–883.

Ansari, A., Ali, A., Asif, M. & Shamsuzzaman (2017). *New J. Chem.* **41**, 16–41.

Bassyouni, F., El Din Gaffer, A., Roaiah, H., El-Senousy, W. M., El Nakkady, S. S. & &Rehim, M. A. (2016). *Res. J. Pharm. Biol. Chem. Sci*, **7**, 24–37.

Bruker (20014). *COLLECT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burch, J. D., Barrett, K., Chen, Y., DeVoss, J., Eigenbrot, C., Goldsmith, R., Ismaili, M. H. A., Lau, K., Lin, Z., Ortwine, D. F., Zarrin, A. A., McEwan, P. A., Barker, J. J., Ellebrandt, C., Kordt, D., Stein, D. B., Wang, X., Chen, Y., Hu, B., Xu, X., Yuen, P.-W., Zhang, Y. & Pei, Z. (2015). *J. Med. Chem.* **58**, 3806–3816.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.

Claramunt, R. M., López, C., Pérez-Medina, C., Pinilla, E., Torres, M. R. & Elguero, J. (2006). *Tetrahedron*, **62**, 11704–11713.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Faidallah, H. M., Khan, K. A., Rostom, S. A. F. & Asiri, A. M. (2013). *J. Enzyme Inhib. Med. Chem.* **28**, 495–508.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gaikwad, D. D., Chapolikar, A. D., Devkate, C. G., Warad, K. D., Tayade, A. P., Pawar, R. P. & Domb, A. J. (2015). *Eur. J. Med. Chem.* **90**, 707–731.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Guo, S., Song, Y., Huang, Q., Yuan, H., Wan, B., Wang, Y., He, R., Beconi, M. G., Franzblau, S. G. & Kozikowski, A. P. (2010). *J. Med. Chem.* **53**, 649–659.

Heifetz, A., Trani, G., Aldeghi, M., MacKinnon, C. H., McEwan, P. A., Brookfield, F. A., Chudyk, E. I., Bodkin, M., Pei, Z., Burch, J. D. & Ortwine, D. F. (2016). *J. Med. Chem.* **59**, 4352–4363.

Jia, J., Xu, Q.-C., Li, R.-C., Tang, X., He, Y.-F., Zhang, M.-Y., Zhang, Y. & Xing, G.-W. (2012). *Org. Biomol. Chem.* **10**, 6279–6286.

Khlebnicova, T. S., Piven, Y. A., Baranovsky, A. V., Lakhvich, F. A., Shishkina, S. V., Zicāne, D., Tetere, Z., Rāviņa, I., Kumpiņš, V., Rijkure, I., Mieriņa, I., Peipiņš, U. & Turks, M. (2017). *Steroids*, **117**, 77–89.

Khlebnikova, T. S., Piven', Y. A., Baranovskii, A. V. & Lakhvich, F. A. (2012). *Russ. J. Org. Chem.* **48**, 411–418.

Kim, J., Song, H. & Park, S. B. (2010). *Eur. J. Org. Chem.* pp. 3815–3822.

Matthews, J. M., McNally, J. J., Connolly, P. J., Xia, M., Zhu, B., Black, S., Chen, C., Hou, C., Liang, Y., Tang, Y. & Macielag, M. J. (2016). *Bioorg. Med. Chem. Lett.* **26**, 5346–5349.

Murugavel, K., Amirthaganesan, S. & R. T. S. (2010). *Chem. Heterocycl. C.* **46**, 302–306.

Nakhai, A. & Bergman, J. (2009). *Tetrahedron*, **65**, 2298–2306.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Polo, E., Trilleras, J., Ramos, J., Galdámez, A., Quiroga, J. & Gutierrez, M. (2016). *Molecules*, **21**, article number 903.

Scala, A., Piperno, A., Risitano, F., Cirmi, S., Navarra, M. & Grassi, G. (2015). *Mol. Divers.* **19**, 473–480.

Sheldrick, G. M. (2015). *Acta Cryst*. C**71**, 3–8.
Silva, V. L. M., Silva, A. M. S., Pinto, D. C. G. A. & Cavaleiro, J. (2006). *Synlett*, pp. 1369–1373.
Song, H., Lee, H., Kim, J. & Park, S. B. (2012). *ACS Comb. Sci.* **14**, 66–74.
Strakova, I., Kumpiņa, I., Rjabovs, V., Luginina, J., Belyakov, S. & Turks, M. (2011). *Tetrahedron Asymmetry*, **22**, 728–739.
Strakova, I., Turks, M. & Strakovs, A. (2009). *Tetrahedron Lett.* **50**, 3046–3049.
Turks, M., Strakova, I., Gorovojs, K., Belyakov, S., Piven, Y. A., Khlebnicova, T. S. & Lakhvich, F. A. (2012). *Tetrahedron*, **68**, 6131–6140.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wiener, J. J. M., Gomez, L., Venkatesan, H., Santillán, A. Jr, Allison, B. D., Schwarz, K. L., Shinde, S., Tang, L., Hack, M. D., Morrow, B. J., Motley, S. T., Goldschmidt, R. M., Shaw, K. J., Jones, T. K. & Grice, C. A. (2007). *Bioorg. Med. Chem. Lett.* **17**, 2718–2722.
Wu, Z.-W., Song, S.-Y., Li, L., Lu, H.-L., Lieberman, B., Huang, Y.-S. & Mach, R. H. (2015). *Bioorg. Med. Chem.* **23**, 1463–1471.

supporting information

Acta Cryst. (2017). E**73**, 1931-1936 [https://doi.org/10.1107/S205698901701667X]

Crystal structure of 3,6,6-trimethyl-4-oxo-1-(pyridin-2-yl)-4,5,6,7-tetrahydro-1*H*-indazol-7-aminium chloride and its monohydrate

Anatoly Mishnev, Alvis Mengots and Māris Turks

Computing details

For both structures, data collection: *COLLECT* (Bruker, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

3,6,6-Trimethyl-4-oxo-1-(pyridin-2-yl)-4,5,6,7-tetrahydro-1*H*-indazol-7-aminium chloride (1)

Crystal data

$C_{15}H_{19}N_4O^+\cdot Cl^-$
M_r = 306.79
Monoclinic, $P2_1/c$
a = 13.5411 (4) Å
b = 7.7421 (2) Å
c = 19.2457 (5) Å
β = 130.493 (2)°
V = 1534.39 (8) Å^3
Z = 4
$F(000)$ = 648
D_x = 1.328 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6801 reflections
θ = 1.0–27.5°
μ = 0.25 mm^{-1}
T = 190 K
Block, colourless
0.38 × 0.32 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
CCD scans
5860 measured reflections
3486 independent reflections
2715 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −17→17
k = −10→9
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.101
S = 1.03
3486 reflections
205 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.7495P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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}
Cl1	0.63264 (4)	0.65297 (6)	0.33536 (3)	0.03342 (14)
O1	0.98736 (12)	−0.08281 (19)	0.66919 (8)	0.0361 (3)
N3	0.59725 (12)	0.17416 (17)	0.53425 (8)	0.0187 (3)
N4	0.65309 (13)	0.13670 (18)	0.62325 (9)	0.0219 (3)
C4	0.67526 (15)	0.1258 (2)	0.51633 (10)	0.0193 (3)
N2	0.41873 (13)	0.26763 (19)	0.38981 (9)	0.0230 (3)
C12	0.42625 (16)	0.3337 (2)	0.51532 (11)	0.0232 (4)
H12	0.471148	0.327724	0.577688	0.028*
C11	0.47588 (15)	0.2621 (2)	0.47773 (10)	0.0190 (3)
N1	0.55052 (14)	0.0192 (2)	0.35950 (9)	0.0220 (3)
C13	0.30686 (17)	0.4145 (2)	0.45593 (12)	0.0282 (4)
H13	0.267881	0.460408	0.477604	0.034*
C3	0.78494 (15)	0.0540 (2)	0.59559 (10)	0.0211 (3)
C6	0.78026 (16)	0.1295 (2)	0.44709 (11)	0.0246 (4)
C15	0.30553 (16)	0.3529 (2)	0.33478 (12)	0.0276 (4)
H15	0.265092	0.362741	0.273282	0.033*
C8	0.88681 (16)	−0.0231 (2)	0.59948 (11)	0.0244 (4)
C5	0.65109 (15)	0.1485 (2)	0.42887 (10)	0.0207 (3)
H5	0.616867	0.265008	0.405413	0.025*
C2	0.76718 (16)	0.0664 (2)	0.66070 (11)	0.0224 (4)
C10	0.75046 (18)	0.1108 (3)	0.35558 (12)	0.0325 (4)
H10A	0.830139	0.113448	0.366104	0.049*
H10B	0.695686	0.204248	0.315864	0.049*
H10C	0.706960	0.002985	0.327613	0.049*
C14	0.24569 (17)	0.4268 (2)	0.36430 (13)	0.0297 (4)
H14	0.166419	0.483251	0.323640	0.036*
C7	0.85647 (16)	−0.0288 (2)	0.50865 (11)	0.0253 (4)
H7A	0.806434	−0.132217	0.476113	0.030*
H7B	0.937384	−0.037310	0.520035	0.030*
C1	0.85803 (17)	0.0141 (3)	0.75907 (11)	0.0312 (4)
H1A	0.809647	−0.005846	0.778844	0.047*
H1B	0.920174	0.104542	0.795200	0.047*
H1C	0.902572	−0.089806	0.766326	0.047*
C9	0.86206 (17)	0.2931 (2)	0.49510 (13)	0.0301 (4)
H9A	0.815252	0.391477	0.456570	0.045*
H9B	0.942494	0.281965	0.507027	0.045*
H9C	0.879617	0.308100	0.551734	0.045*
H1N1	0.487 (2)	0.000 (3)	0.3670 (14)	0.046 (6)*
H2N1	0.503 (2)	0.062 (3)	0.2980 (16)	0.054 (7)*

H3N1	0.584 (2)	−0.088 (3)	0.3627 (14)	0.042 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0363 (3)	0.0353 (3)	0.0225 (2)	0.0052 (2)	0.01632 (19)	−0.00482 (19)
O1	0.0235 (7)	0.0442 (8)	0.0281 (6)	0.0113 (6)	0.0113 (6)	0.0038 (6)
N3	0.0190 (7)	0.0211 (7)	0.0168 (6)	0.0005 (6)	0.0119 (5)	0.0004 (6)
N4	0.0244 (7)	0.0234 (7)	0.0184 (6)	−0.0002 (6)	0.0141 (6)	0.0012 (6)
C4	0.0189 (8)	0.0186 (8)	0.0210 (7)	−0.0011 (6)	0.0132 (7)	−0.0020 (7)
N2	0.0207 (7)	0.0263 (7)	0.0216 (7)	0.0011 (6)	0.0136 (6)	0.0027 (6)
C12	0.0272 (9)	0.0200 (8)	0.0268 (8)	0.0003 (7)	0.0195 (7)	0.0005 (7)
C11	0.0189 (8)	0.0157 (8)	0.0232 (8)	−0.0015 (6)	0.0140 (7)	−0.0004 (7)
N1	0.0204 (7)	0.0266 (8)	0.0191 (7)	0.0023 (6)	0.0129 (6)	−0.0013 (6)
C13	0.0299 (9)	0.0235 (9)	0.0400 (10)	0.0021 (8)	0.0267 (8)	−0.0010 (8)
C3	0.0187 (8)	0.0209 (8)	0.0194 (7)	−0.0011 (7)	0.0105 (6)	−0.0019 (7)
C6	0.0218 (8)	0.0297 (9)	0.0264 (8)	0.0031 (7)	0.0176 (7)	0.0007 (8)
C15	0.0230 (8)	0.0299 (9)	0.0252 (8)	0.0022 (8)	0.0136 (7)	0.0063 (8)
C8	0.0203 (8)	0.0213 (8)	0.0254 (8)	−0.0005 (7)	0.0122 (7)	−0.0016 (7)
C5	0.0205 (8)	0.0220 (8)	0.0212 (7)	0.0022 (7)	0.0143 (7)	0.0010 (7)
C2	0.0214 (8)	0.0212 (8)	0.0201 (8)	−0.0022 (7)	0.0114 (7)	−0.0010 (7)
C10	0.0285 (9)	0.0455 (12)	0.0315 (9)	0.0064 (9)	0.0230 (8)	0.0043 (9)
C14	0.0224 (9)	0.0245 (9)	0.0379 (10)	0.0048 (7)	0.0176 (8)	0.0055 (8)
C7	0.0198 (8)	0.0281 (9)	0.0290 (9)	0.0042 (7)	0.0163 (7)	−0.0020 (8)
C1	0.0291 (9)	0.0364 (11)	0.0205 (8)	0.0007 (8)	0.0127 (8)	0.0025 (8)
C9	0.0251 (9)	0.0299 (10)	0.0390 (10)	0.0022 (8)	0.0224 (8)	0.0014 (8)

Geometric parameters (Å, º)

O1—C8	1.223 (2)	C6—C10	1.537 (2)
N3—C4	1.360 (2)	C6—C7	1.544 (2)
N3—N4	1.3811 (18)	C6—C5	1.552 (2)
N3—C11	1.424 (2)	C15—C14	1.380 (3)
N4—C2	1.325 (2)	C15—H15	0.9300
C4—C3	1.378 (2)	C8—C7	1.515 (2)
C4—C5	1.502 (2)	C5—H5	0.9800
N2—C11	1.328 (2)	C2—C1	1.496 (2)
N2—C15	1.341 (2)	C10—H10A	0.9600
C12—C13	1.383 (2)	C10—H10B	0.9600
C12—C11	1.383 (2)	C10—H10C	0.9600
C12—H12	0.9300	C14—H14	0.9300
N1—C5	1.509 (2)	C7—H7A	0.9700
N1—H1N1	0.97 (2)	C7—H7B	0.9700
N1—H2N1	0.97 (2)	C1—H1A	0.9600
N1—H3N1	0.93 (2)	C1—H1B	0.9600
C13—C14	1.381 (3)	C1—H1C	0.9600
C13—H13	0.9300	C9—H9A	0.9600
C3—C2	1.424 (2)	C9—H9B	0.9600

C3—C8	1.459 (2)	C9—H9C	0.9600
C6—C9	1.535 (3)		

C4—N3—N4	111.53 (12)	C3—C8—C7	114.43 (14)
C4—N3—C11	129.76 (13)	C4—C5—N1	109.18 (13)
N4—N3—C11	118.61 (12)	C4—C5—C6	110.02 (13)
C2—N4—N3	105.47 (13)	N1—C5—C6	111.99 (13)
N3—C4—C3	106.66 (13)	C4—C5—H5	108.5
N3—C4—C5	127.76 (14)	N1—C5—H5	108.5
C3—C4—C5	125.56 (14)	C6—C5—H5	108.5
C11—N2—C15	116.33 (14)	N4—C2—C3	110.63 (14)
C13—C12—C11	116.96 (15)	N4—C2—C1	120.64 (15)
C13—C12—H12	121.5	C3—C2—C1	128.72 (16)
C11—C12—H12	121.5	C6—C10—H10A	109.5
N2—C11—C12	125.07 (15)	C6—C10—H10B	109.5
N2—C11—N3	114.67 (13)	H10A—C10—H10B	109.5
C12—C11—N3	120.26 (14)	C6—C10—H10C	109.5
C5—N1—H1N1	110.3 (13)	H10A—C10—H10C	109.5
C5—N1—H2N1	110.9 (14)	H10B—C10—H10C	109.5
H1N1—N1—H2N1	106.3 (18)	C15—C14—C13	118.12 (16)
C5—N1—H3N1	114.2 (13)	C15—C14—H14	120.9
H1N1—N1—H3N1	107.5 (19)	C13—C14—H14	120.9
H2N1—N1—H3N1	107.3 (19)	C8—C7—C6	114.06 (14)
C14—C13—C12	119.76 (16)	C8—C7—H7A	108.7
C14—C13—H13	120.1	C6—C7—H7A	108.7
C12—C13—H13	120.1	C8—C7—H7B	108.7
C4—C3—C2	105.68 (14)	C6—C7—H7B	108.7
C4—C3—C8	121.68 (14)	H7A—C7—H7B	107.6
C2—C3—C8	132.55 (15)	C2—C1—H1A	109.5
C9—C6—C10	108.51 (15)	C2—C1—H1B	109.5
C9—C6—C7	109.37 (14)	H1A—C1—H1B	109.5
C10—C6—C7	110.59 (14)	C2—C1—H1C	109.5
C9—C6—C5	108.97 (14)	H1A—C1—H1C	109.5
C10—C6—C5	109.35 (13)	H1B—C1—H1C	109.5
C7—C6—C5	110.02 (14)	C6—C9—H9A	109.5
N2—C15—C14	123.68 (16)	C6—C9—H9B	109.5
N2—C15—H15	118.2	H9A—C9—H9B	109.5
C14—C15—H15	118.2	C6—C9—H9C	109.5
O1—C8—C3	123.57 (16)	H9A—C9—H9C	109.5
O1—C8—C7	121.97 (15)	H9B—C9—H9C	109.5

C4—N3—N4—C2	0.69 (18)	N3—C4—C5—N1	−74.7 (2)
C11—N3—N4—C2	−176.00 (14)	C3—C4—C5—N1	107.05 (18)
N4—N3—C4—C3	0.27 (18)	N3—C4—C5—C6	162.06 (16)
C11—N3—C4—C3	176.49 (15)	C3—C4—C5—C6	−16.2 (2)
N4—N3—C4—C5	−178.26 (15)	C9—C6—C5—C4	−74.59 (17)
C11—N3—C4—C5	−2.0 (3)	C10—C6—C5—C4	166.95 (14)
C15—N2—C11—C12	1.4 (2)	C7—C6—C5—C4	45.31 (18)

C15—N2—C11—N3	−178.55 (14)	C9—C6—C5—N1	163.80 (14)
C13—C12—C11—N2	1.1 (3)	C10—C6—C5—N1	45.35 (19)
C13—C12—C11—N3	−178.92 (15)	C7—C6—C5—N1	−76.29 (16)
C4—N3—C11—N2	14.7 (2)	N3—N4—C2—C3	−1.36 (18)
N4—N3—C11—N2	−169.29 (14)	N3—N4—C2—C1	177.90 (15)
C4—N3—C11—C12	−165.27 (16)	C4—C3—C2—N4	1.55 (19)
N4—N3—C11—C12	10.7 (2)	C8—C3—C2—N4	−174.86 (17)
C11—C12—C13—C14	−2.6 (3)	C4—C3—C2—C1	−177.64 (17)
N3—C4—C3—C2	−1.05 (18)	C8—C3—C2—C1	6.0 (3)
C5—C4—C3—C2	177.52 (15)	N2—C15—C14—C13	1.0 (3)
N3—C4—C3—C8	175.84 (15)	C12—C13—C14—C15	1.7 (3)
C5—C4—C3—C8	−5.6 (3)	O1—C8—C7—C6	−145.62 (17)
C11—N2—C15—C14	−2.5 (3)	C3—C8—C7—C6	36.1 (2)
C4—C3—C8—O1	177.45 (17)	C9—C6—C7—C8	62.12 (18)
C2—C3—C8—O1	−6.6 (3)	C10—C6—C7—C8	−178.44 (14)
C4—C3—C8—C7	−4.4 (2)	C5—C6—C7—C8	−57.54 (19)
C2—C3—C8—C7	171.59 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···Cl1^{i}	0.93	2.80	3.4470 (17)	127
C14—H14···O1^{ii}	0.93	2.44	3.277 (2)	150
C7—H7*A*···Cl1^{iii}	0.97	2.71	3.6401 (18)	160
C1—H1*B*···O1^{iv}	0.96	2.60	3.503 (2)	156
N1—H1*N*1···N4^{v}	0.97 (2)	2.29 (2)	3.218 (2)	161 (2)
N1—H1*N*1···N2	0.97 (2)	2.42 (2)	2.928 (2)	112 (2)
N1—H2*N*1···Cl1^{vi}	0.97 (2)	2.08 (2)	3.034 (2)	168 (2)
N1—H3*N*1···Cl1^{iii}	0.93 (2)	2.27 (2)	3.188 (2)	167 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, −*y*+1/2, *z*−1/2; (iii) *x*, *y*−1, *z*; (iv) −*x*+2, *y*+1/2, −*z*+3/2; (v) −*x*+1, −*y*, −*z*+1; (vi) −*x*+1, *y*−1/2, −*z*+1/2.

3,6,6-Trimethyl-4-oxo-1-(pyridin-2-yl)-4,5,6,7-tetrahydro-1*H*-indazol-7-aminium chloride monohydrate (2)

Crystal data

$C_{15}H_{19}N_4O^+·Cl^-·H_2O$
M_r = 324.81
Monoclinic, $P2_1/c$
a = 10.1855 (2) Å
b = 7.4951 (2) Å
c = 20.7961 (4) Å
β = 100.545 (1)°
V = 1560.79 (6) Å^3
Z = 4

$F(000)$ = 688
D_x = 1.382 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8626 reflections
θ = 1.0–27.5°
μ = 0.26 mm^{-1}
T = 190 K
Block, colourless
0.42 × 0.25 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
CCD scans

5549 measured reflections
3552 independent reflections
2874 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

θ_{max} = 27.7°, θ_{min} = 3.6°
h = −13→13
k = −9→9
l = −27→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
S = 1.06
3552 reflections
222 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.794P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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}
Cl1	0.06154 (4)	0.62526 (6)	0.39636 (2)	0.02975 (13)
O1	0.45919 (12)	−0.12171 (17)	0.26173 (5)	0.0286 (3)
N2	0.33632 (13)	0.28400 (18)	0.51823 (6)	0.0210 (3)
O1W	−0.00940 (13)	0.25508 (19)	0.46352 (7)	0.0328 (3)
N3	0.48296 (12)	0.17260 (17)	0.45521 (6)	0.0159 (3)
N1	0.18153 (14)	0.01688 (19)	0.43612 (7)	0.0183 (3)
N4	0.61172 (12)	0.13967 (18)	0.44629 (6)	0.0196 (3)
C5	0.24311 (14)	0.1376 (2)	0.39147 (7)	0.0155 (3)
H5	0.223932	0.261303	0.401963	0.019*
C12	0.57141 (16)	0.3394 (2)	0.55440 (8)	0.0219 (3)
H12	0.658465	0.326736	0.547312	0.026*
C11	0.46319 (15)	0.2686 (2)	0.51150 (7)	0.0174 (3)
C4	0.39179 (14)	0.1150 (2)	0.40322 (7)	0.0153 (3)
C6	0.18454 (15)	0.1060 (2)	0.31807 (7)	0.0176 (3)
C10	0.03220 (16)	0.0870 (2)	0.30801 (8)	0.0246 (4)
H10A	0.009876	−0.020414	0.328751	0.037*
H10B	−0.003916	0.081667	0.262056	0.037*
H10C	−0.004705	0.187831	0.326935	0.037*
C9	0.21584 (16)	0.2703 (2)	0.27933 (8)	0.0227 (3)
H9A	0.180810	0.375246	0.296617	0.034*
H9B	0.175456	0.256460	0.234144	0.034*
H9C	0.310786	0.282002	0.283039	0.034*
C3	0.46350 (15)	0.0404 (2)	0.35966 (7)	0.0166 (3)
C8	0.39804 (16)	−0.0515 (2)	0.30028 (7)	0.0192 (3)
C15	0.31230 (18)	0.3783 (2)	0.56960 (8)	0.0270 (4)
H15	0.224058	0.395222	0.574240	0.032*
C7	0.24693 (16)	−0.0608 (2)	0.29224 (7)	0.0213 (3)
H7A	0.223032	−0.164981	0.315275	0.026*

H7B	0.209284	−0.075806	0.246229	0.026*
C14	0.4120 (2)	0.4514 (2)	0.61590 (8)	0.0299 (4)
H14	0.391561	0.513786	0.651450	0.036*
C13	0.54279 (19)	0.4297 (2)	0.60821 (8)	0.0280 (4)
H13	0.611825	0.475897	0.639260	0.034*
C2	0.59994 (15)	0.0631 (2)	0.38810 (7)	0.0196 (3)
C1	0.72083 (17)	0.0203 (3)	0.36008 (9)	0.0295 (4)
H1A	0.799516	0.046429	0.391767	0.044*
H1B	0.720784	0.090854	0.321550	0.044*
H1C	0.720059	−0.104005	0.348878	0.044*
H1W	−0.026 (3)	0.288 (4)	0.4977 (14)	0.063 (9)*
H2W	0.012 (3)	0.362 (4)	0.4440 (13)	0.066 (8)*
H1N1	0.1557 (19)	−0.083 (3)	0.4188 (9)	0.024 (5)*
H2N1	0.244 (2)	−0.009 (3)	0.4766 (11)	0.036 (5)*
H3N1	0.112 (2)	0.080 (3)	0.4513 (11)	0.049 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0343 (2)	0.0261 (2)	0.0301 (2)	−0.00602 (18)	0.00909 (17)	−0.00145 (17)
O1	0.0328 (7)	0.0360 (7)	0.0182 (6)	0.0076 (5)	0.0077 (5)	−0.0040 (5)
N2	0.0237 (7)	0.0214 (7)	0.0185 (6)	0.0011 (6)	0.0053 (5)	−0.0027 (6)
O1W	0.0343 (7)	0.0287 (7)	0.0385 (8)	0.0014 (6)	0.0152 (6)	−0.0051 (6)
N3	0.0144 (6)	0.0174 (6)	0.0156 (6)	−0.0002 (5)	0.0018 (5)	0.0000 (5)
N1	0.0185 (7)	0.0208 (7)	0.0162 (6)	−0.0037 (6)	0.0045 (5)	−0.0014 (6)
N4	0.0140 (6)	0.0226 (7)	0.0222 (7)	0.0005 (5)	0.0036 (5)	0.0019 (6)
C5	0.0155 (7)	0.0168 (7)	0.0143 (7)	−0.0016 (6)	0.0026 (5)	0.0007 (6)
C12	0.0250 (8)	0.0171 (7)	0.0211 (8)	−0.0021 (6)	−0.0029 (6)	0.0022 (6)
C11	0.0226 (8)	0.0141 (7)	0.0147 (7)	−0.0004 (6)	0.0018 (6)	0.0019 (6)
C4	0.0164 (7)	0.0153 (7)	0.0138 (7)	−0.0017 (6)	0.0022 (5)	0.0020 (6)
C6	0.0156 (7)	0.0224 (8)	0.0140 (7)	−0.0015 (6)	0.0003 (5)	0.0008 (6)
C10	0.0177 (8)	0.0332 (9)	0.0216 (8)	−0.0044 (7)	−0.0002 (6)	−0.0003 (7)
C9	0.0221 (8)	0.0251 (9)	0.0193 (7)	−0.0006 (7)	−0.0004 (6)	0.0054 (7)
C3	0.0185 (7)	0.0171 (7)	0.0146 (7)	0.0000 (6)	0.0039 (6)	0.0017 (6)
C8	0.0262 (8)	0.0180 (7)	0.0139 (7)	0.0015 (6)	0.0045 (6)	0.0031 (6)
C15	0.0344 (9)	0.0263 (9)	0.0222 (8)	0.0030 (7)	0.0100 (7)	−0.0024 (7)
C7	0.0244 (8)	0.0229 (8)	0.0163 (7)	−0.0042 (7)	0.0033 (6)	−0.0034 (6)
C14	0.0506 (12)	0.0225 (9)	0.0173 (7)	−0.0006 (8)	0.0079 (7)	−0.0035 (7)
C13	0.0427 (11)	0.0181 (8)	0.0189 (8)	−0.0055 (7)	−0.0061 (7)	−0.0014 (7)
C2	0.0183 (8)	0.0210 (8)	0.0201 (7)	0.0016 (6)	0.0054 (6)	0.0036 (6)
C1	0.0205 (8)	0.0392 (11)	0.0310 (9)	0.0027 (8)	0.0109 (7)	0.0000 (8)

Geometric parameters (Å, º)

O1—C8	1.2207 (19)	C6—C7	1.543 (2)
N2—C11	1.330 (2)	C10—H10A	0.9600
N2—C15	1.340 (2)	C10—H10B	0.9600
O1W—H1W	0.80 (3)	C10—H10C	0.9600

O1W—H2W	0.94 (3)	C9—H9A	0.9600
N3—C4	1.3601 (18)	C9—H9B	0.9600
N3—N4	1.3800 (17)	C9—H9C	0.9600
N3—C11	1.4196 (19)	C3—C2	1.418 (2)
N1—C5	1.5127 (19)	C3—C8	1.464 (2)
N1—H1N1	0.85 (2)	C8—C7	1.519 (2)
N1—H2N1	0.98 (2)	C15—C14	1.378 (3)
N1—H3N1	0.95 (2)	C15—H15	0.9300
N4—C2	1.325 (2)	C7—H7A	0.9700
C5—C4	1.499 (2)	C7—H7B	0.9700
C5—C6	1.5522 (19)	C14—C13	1.380 (3)
C5—H5	0.9800	C14—H14	0.9300
C12—C13	1.384 (2)	C13—H13	0.9300
C12—C11	1.390 (2)	C2—C1	1.491 (2)
C12—H12	0.9300	C1—H1A	0.9600
C4—C3	1.382 (2)	C1—H1B	0.9600
C6—C10	1.534 (2)	C1—H1C	0.9600
C6—C9	1.537 (2)		

C11—N2—C15	116.89 (14)	H10B—C10—H10C	109.5
H1W—O1W—H2W	103 (3)	C6—C9—H9A	109.5
C4—N3—N4	111.34 (12)	C6—C9—H9B	109.5
C4—N3—C11	129.57 (13)	H9A—C9—H9B	109.5
N4—N3—C11	118.90 (12)	C6—C9—H9C	109.5
C5—N1—H1N1	113.5 (13)	H9A—C9—H9C	109.5
C5—N1—H2N1	111.4 (12)	H9B—C9—H9C	109.5
H1N1—N1—H2N1	106.9 (18)	C4—C3—C2	105.85 (13)
C5—N1—H3N1	108.9 (15)	C4—C3—C8	122.00 (13)
H1N1—N1—H3N1	112.7 (19)	C2—C3—C8	132.00 (14)
H2N1—N1—H3N1	102.9 (18)	O1—C8—C3	123.26 (15)
C2—N4—N3	105.71 (12)	O1—C8—C7	122.43 (14)
C4—C5—N1	110.64 (12)	C3—C8—C7	114.23 (13)
C4—C5—C6	109.76 (12)	N2—C15—C14	123.21 (17)
N1—C5—C6	112.59 (12)	N2—C15—H15	118.4
C4—C5—H5	107.9	C14—C15—H15	118.4
N1—C5—H5	107.9	C8—C7—C6	113.45 (13)
C6—C5—H5	107.9	C8—C7—H7A	108.9
C13—C12—C11	116.49 (16)	C6—C7—H7A	108.9
C13—C12—H12	121.8	C8—C7—H7B	108.9
C11—C12—H12	121.8	C6—C7—H7B	108.9
N2—C11—C12	124.81 (14)	H7A—C7—H7B	107.7
N2—C11—N3	114.70 (13)	C15—C14—C13	118.40 (16)
C12—C11—N3	120.48 (14)	C15—C14—H14	120.8
N3—C4—C3	106.48 (13)	C13—C14—H14	120.8
N3—C4—C5	128.05 (13)	C14—C13—C12	120.12 (16)
C3—C4—C5	125.34 (13)	C14—C13—H13	119.9
C10—C6—C9	107.73 (13)	C12—C13—H13	119.9
C10—C6—C7	110.38 (13)	N4—C2—C3	110.57 (13)

C9—C6—C7	109.20 (12)	N4—C2—C1	120.48 (14)
C10—C6—C5	110.21 (12)	C3—C2—C1	128.90 (15)
C9—C6—C5	108.27 (12)	C2—C1—H1A	109.5
C7—C6—C5	110.96 (12)	C2—C1—H1B	109.5
C6—C10—H10A	109.5	H1A—C1—H1B	109.5
C6—C10—H10B	109.5	C2—C1—H1C	109.5
H10A—C10—H10B	109.5	H1A—C1—H1C	109.5
C6—C10—H10C	109.5	H1B—C1—H1C	109.5
H10A—C10—H10C	109.5		

C4—N3—N4—C2	0.70 (17)	N3—C4—C3—C2	−1.90 (16)
C11—N3—N4—C2	−174.73 (13)	C5—C4—C3—C2	174.12 (14)
C15—N2—C11—C12	1.5 (2)	N3—C4—C3—C8	174.09 (13)
C15—N2—C11—N3	−178.02 (14)	C5—C4—C3—C8	−9.9 (2)
C13—C12—C11—N2	1.0 (2)	C4—C3—C8—O1	−178.45 (15)
C13—C12—C11—N3	−179.50 (14)	C2—C3—C8—O1	−3.6 (3)
C4—N3—C11—N2	9.7 (2)	C4—C3—C8—C7	−1.5 (2)
N4—N3—C11—N2	−175.82 (13)	C2—C3—C8—C7	173.30 (16)
C4—N3—C11—C12	−169.86 (15)	C11—N2—C15—C14	−2.8 (2)
N4—N3—C11—C12	4.6 (2)	O1—C8—C7—C6	−148.01 (15)
N4—N3—C4—C3	0.81 (17)	C3—C8—C7—C6	35.01 (18)
C11—N3—C4—C3	175.62 (14)	C10—C6—C7—C8	179.76 (13)
N4—N3—C4—C5	−175.06 (14)	C9—C6—C7—C8	61.51 (16)
C11—N3—C4—C5	−0.3 (2)	C5—C6—C7—C8	−57.76 (16)
N1—C5—C4—N3	−72.98 (19)	N2—C15—C14—C13	1.5 (3)
C6—C5—C4—N3	162.17 (14)	C15—C14—C13—C12	1.2 (3)
N1—C5—C4—C3	111.88 (16)	C11—C12—C13—C14	−2.3 (2)
C6—C5—C4—C3	−13.0 (2)	N3—N4—C2—C3	−1.93 (17)
C4—C5—C6—C10	167.33 (13)	N3—N4—C2—C1	175.62 (15)
N1—C5—C6—C10	43.61 (17)	C4—C3—C2—N4	2.45 (18)
C4—C5—C6—C9	−75.07 (15)	C8—C3—C2—N4	−172.97 (15)
N1—C5—C6—C9	161.21 (13)	C4—C3—C2—C1	−174.84 (17)
C4—C5—C6—C7	44.75 (16)	C8—C3—C2—C1	9.7 (3)
N1—C5—C6—C7	−78.96 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···Cl1^{i}	0.93	2.90	3.7006 (17)	145
C14—H14···O1^{ii}	0.93	2.41	3.244 (2)	149
O1*W*—H1*W*···Cl1^{iii}	0.80 (3)	2.39 (3)	3.185 (2)	176 (3)
O1*W*—H2*W*···Cl1	0.94 (3)	2.31 (3)	3.247 (2)	179 (2)
N1—H1*N*1···Cl1^{iv}	0.85 (2)	2.40 (2)	3.228 (2)	165 (2)
N1—H2*N*1···N4^{v}	0.98 (2)	2.20 (2)	3.1475 (19)	164 (2)
N1—H3*N*1···O1*W*	0.95 (2)	1.85 (3)	2.775 (2)	162 (2)

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