1-Hydrazinophthalazine Hydrochloride

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Abstract. $C_8H_8N_4 \cdot HCl$, space group $P2_1/c$ with $a = 9.408$ (2), $b = 14.592$ (2), $c = 6.643$ (2) Å, $\beta = 103.59$ (2)°; $Z = 4$, $D_x = 1.473$ and $D_m = 1.486$ g cm^{-3}. The structure was solved by an image-seeking method and refined to $R = 0.109$ for 1234 counter-collected data. The cation has an additional H at N(2) relative to phthalazine. The crystal structure is stabilized by hydrogen bonding and by ring stacking, with a separation of 3.32 Å, along [001] between glide-plane-related molecules.

Introduction. The title compound (I) is used in the treatment of hypertension as Hydralazine or Apresoline. Its hypotensive and antihypertensive properties make it one of the direct-acting vasodilators (Druey & Tripod, 1967; Rossi, 1975).

(I)
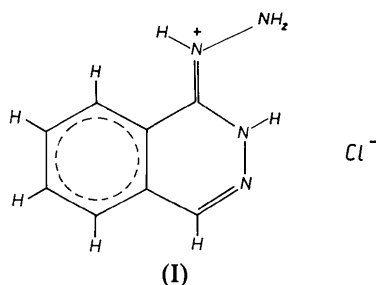
(I) crystallizes from aqueous solution by slow evaporation as very fine pale-yellow single crystals, needle shaped, often overgrown. Systematic absences: 0k0, k odd and h0l, l odd indicating space group $P2_1/c$, were observed on the Weissenberg photographs. The intensity data were collected with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation on a crystal of dimensions 0.10 × 0.05 × 0.09 mm. The cell parameters were obtained by least-squares refinement from the setting angles of 15 strong reflexions used in the auto-indexing procedure (Chojnacki, Lebioda & Stadnicka, 1975). Intensity measurements were carried out up to $\theta = 30°$ using the θ–2θ scan mode and (0.6 + tan θ)° scan range. Lorentz and polarization corrections were applied. No correction was made for absorption [μ(Mo $K\alpha$) = 3.80 cm^{-1}]. The variation in the intensity of the standard reflexion, recorded after each group of 47 measurements, was less than 3%. Of 2567 measured indepen-

dent reflexions, 543 had $I < 0$. The structure was solved using minimum image-seeking functions of the second and fourth order on a Patterson map. The structure

Table 1. *The final atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$), *with their estimated standard deviations in parentheses*

	X/a	Y/b	Z/c
Cl	−1820 (2)	8654 (1)	−856 (3)
N(2)	1854 (6)	5814 (4)	258 (9)
N(3)	3284 (6)	5503 (4)	714 (9)
N(4)	−3 (5)	6855 (3)	−275 (9)
N(5)	−1018 (6)	6105 (3)	−603 (9)
C(1)	1402 (7)	6678 (4)	142 (12)
C(4)	4270 (8)	6138 (4)	996 (11)
C(5)	5083 (8)	7766 (5)	1232 (12)
C(6)	4735 (9)	8687 (6)	1122 (12)
C(7)	3280 (8)	8974 (5)	721 (12)
C(8)	2138 (8)	8341 (5)	385 (12)
C(9)	2504 (7)	7402 (4)	466 (10)
C(10)	3972 (7)	7115 (5)	921 (10)
H(1)	517 (7)	587 (5)	133 (10)
H(2)	598 (8)	756 (5)	156 (10)
H(3)	548 (3)	904 (3)	130 (3)
H(4)	306 (7)	960 (5)	63 (10)
H(5)	110 (3)	850 (3)	−16 (3)
H(6)	131 (7)	538 (5)	−7 (10)
H(7)	−38 (3)	739 (3)	−43 (3)
H(8)	−163 (3)	624 (3)	63 (3)
H(9)	−170 (3)	627 (3)	−218 (3)

Table 2. *The deviations* (Å) *of the atoms from the phthalazine best plane*

The equation of the plane is
$(-1.9634)x + (-0.0255)y + (6.6406)z = (-0.1950)$.

C(1)	−0.003*		
N(2)	−0.013*	H(6)	−0.122
N(3)	−0.010*		
C(4)	0.002*	H(1)	0.047
C(5)	−0.005*	H(2)	0.038
C(6)	−0.012*	H(3)	−0.041
C(7)	0.007*	H(4)	−0.012
C(8)	0.010*	H(5)	−0.149
C(9)	−0.006*		
C(10)	0.009*		
N(4)	−0.005	H(7)	−0.035
N(5)	−0.021	H(8)	0.918
		H(9)	−0.935
Cl⁻	−0.038		

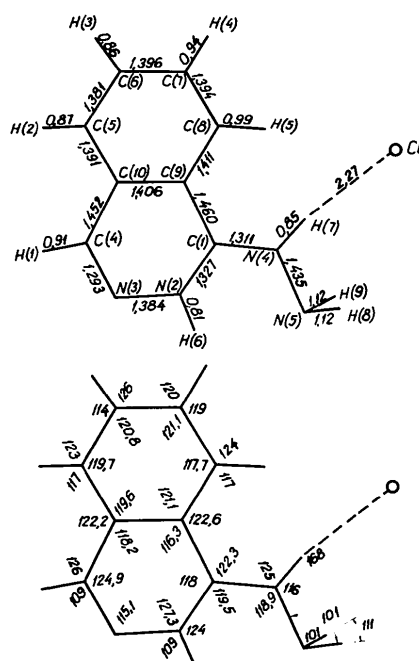* Atom used in the plane calculation.

Fig. 1. Bond lengths (Å) and angles (°) in the molecule. E.s.d.'s for those involving non-hydrogen atoms only are on average 0·009 Å and 0·6°, for the others 0·07 Å and 4°, respectively. The shortest N–H···Cl⁻ hydrogen bond is marked by a dashed line.
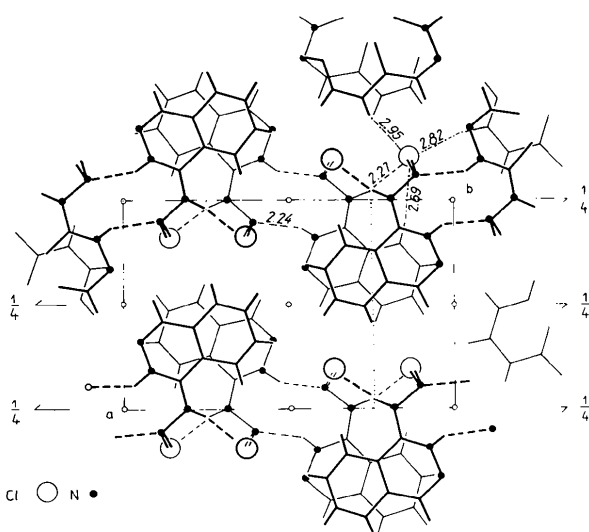

Fig. 2. Projection of the structure viewed along c (– – – – hydrogen bonds, ·–·–·– contacts between Cl⁻ and methine H atoms shorter than 3·00 Å).

was refined by Fourier syntheses and the full-matrix least-squares method using 1234 reflexions with $I > 3\sigma(F_o)$. These calculations were carried out with the *SHELX* program system (Sheldrick, 1975) adapted for use on a Cyber-72 computer. The weighting scheme $w = k[\sigma^2(F_o) + |g|F_o^2]^{-1}$ was used, where k and $|g|$ values

Table 3. *The distances (Å) and angles (°) in the hydrogen-bond system*

The mean values of the e.s.d.'s are 0·008, 0·07 Å and 6° for $D \cdots A$, $H \cdots A$ and $\angle DHA$ respectively.

$D-H\cdots A$	$D\cdots A$	$H\cdots A$	$\angle DHA$
N(2)–H(6)···N(5ⁱ)	2·932	2·24	143
N(4)–H(7)···Clⁱⁱ	3·107	2·27	168
N(5)–H(8)···Clⁱⁱⁱ	3·429	2·39	153
N(5)–H(9)···Clⁱᵛ	3·411	2·42	147
C(8)–H(5)···Clⁱⁱ	3·648	2·69	166
C(7)–H(4)···Clᵛ	3·733	2·82	165
C(5)–H(2)···Clᵛⁱ	3·725	2·95	149

Symmetry code

(i)	$-x$,	$1-y$,	$-z$	(iv)	x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$
(ii)	x,	y,	z	(v)	$-x$, $2-y$, $-z$
(iii)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	(vi)	$1+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$

were refined and converged to 2·545 and 0·00044 respectively. A difference map showed the positions of all H atoms, which were refined with isotropic thermal parameters equivalent to the anisotropic parameters of the atoms to which they were bound. The shifts in the parameters of the final cycle of refinement were less than 0·3 of the e.s.d.'s for non-hydrogen atoms and 0·6 e.s.d. for H. With the final discrepancy indices $R = 0·109$, $R_w = 0·086$ and $R_G = 0·087$, where $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$, $R_G = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, a difference map revealed several randomly distributed peaks of about 0·6 e Å⁻³, which were of no chemical significance. The final atomic positional coordinates and their standard deviations are given in Table 1.*

Discussion. The bond lengths and angles found in this structure are shown in Fig. 1. In comparison with the structure of phthalazine (Huiszoon, van de Waal, van Egmond & Harkema, 1972), there are small differences in bond lengths and valence angles due to the protonation of the phthalazine system at N(2) and the electron-releasing substituent –NH–NH₂ at C(1). The C(1)–N(4) bond length is short relative to the expected value of 1·426 (12) Å (*Molecular Structures and Dimensions*, 1972). The N(4)–N(5) hydrazine bond length of 1·436 (8) Å is similar to those found in N₂H₅Cl (Sakurai & Tomiie, 1952) and in N₂H₅HS (Lazarini & Vardjan-Jarec, 1975).

The phthalazine system is planar (Table 2). The packing in the structure is shown in Fig. 2. The molecules are bonded in pairs by N(2)–H(6)···N(5) hydrogen bonds around the centres of symmetry at

$(0,\frac{1}{2},0)$ and $(0,0,\frac{1}{2})$. Stacking of the glide-plane-related molecules, 3·32 Å apart, is observed along the [001] direction. The N—H$\cdots$Cl$^-$ hydrogen bonds link stacked molecules and infinite chains along the [001] direction are formed. The distances and angles in the system of hydrogen bonds are given in Table 3. The Cl$^-$ anion is the acceptor in three hydrogen bonds; there are also three methine H atoms, H(2), H(4) and H(5), at distances less than 3·00 Å. All four available N-bonded H atoms are involved in hydrogen bonding.

A powdered preparation of the title compound was obtained through the courtesy of POLFA-Pabianice. We thank the X-ray Laboratory of SLAFiBS, Kraków, for making the diffractometer available.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Statistical bias in scaling factors: erratum. By A. J. C. WILSON, *Department of Physics, University of Birmingham, Birmingham B15 2TT, England*

The numerical measures of discrepancy, typically amounting to several per cent, quoted in crystal-structure determinations are not the residuals R_1 and R_2 but their square roots; R_1 and R_2 are thus typically measured in tenths of a per cent. Wilson [*Anomalous Scattering* (1975), edited by S. Ramaseshan & S. C. Abrahams, pp. 325–332. Copenhagen: Munksgaard; T. R. Lomer & A. J. C. Wilson (1975). *Acta Cryst.* **B31**, 646–647] failed to notice this, so that mentions of 'some per cent' in these papers should be read as 'some tenths of a per cent'. Later papers are either adequately vague or unaffected by this misapprehension.

All information is given in the abstract.

Dihydro-6,7 canrénone: erratum. Par EVELYNE SURCOUF, *Laboratoire de Minéralogie–Cristallographie, associé au CNRS, Université Pierre et Marie Curie, Tour* 16, 4 *place Jussieu,* 75230 *Paris CEDEX* 05, *France*

The name of the title compound in the papers by Surcouf [*Acta Cryst.* (1977), **B33**, 3891–3894; (1978), **B34**, 1049] on the steroid SC5233 is in error: For 'Dihydroxy-5,6 Canrénone' read 'Dihydro-6,7 Canrénone'. This compound is a novel steroid from the Searle Laboratories described by J. A. Cella & C. M. Kagawa [*J. Am. Chem. Soc.* (1957), **79**, 4808–4809].

Le résumé contient tous les détails pertinents.