The high value of the R factor results from the poor quality of the crystals. The H atoms attached to N and O atoms were placed at 1.03 Å from the respective parent atom in the direction obtained from the refinement (Taylor & Kennard, 1983).

Program used to solve the structure: *SHELXS*86 (Sheldrick, 1985). Program used for full-matrix least-squares refinement: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3-Diamino-5-hydrophenazinium Chloride Trihydrate

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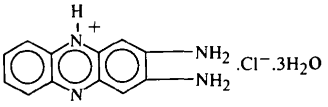
Abstract

The three rings of the phenazinium molecule of the title compound, $C_{12}H_{11}N_4^+.Cl^-.3H_2O$, are all coplanar, and protonation occurs preferentially on an aromatic N atom rather than the amino N atoms. The C—C and C—N bond lengths of the unsubstituted side of the molecule agree closely with those of phenazine, but those on the substituted side differ from those of phenazine and 1,2-benzenediamine.

Comment

In the synthesis of mono-*N*-acetyl-1,2-benzenediamine from acetyl chloride and 1,2-benzenediamine, some red crystalline needles were obtained as a by-product. These were shown *via* single-crystal structure determination to be 2,3-diamino-5-hydrophenazinium chloride trihydrate, (I). It is of interest to note that protonation occurs on a ring N atom rather than an amino N atom. This is consistent with the greater basicity of pyridine (pK = 5.25) compared with aniline (pK = 4.63). The mechanism for the formation of this product is not obvious. However, it has been reported that exposure of 2,3-napthalenediamine to light gives some of the corresponding phenazine (Cukor & Lott, 1965). The same cation, but with perchlorate as anion, was obtained in the cupric chloride oxidation of *o*-phenylenediamine (*i.e.* 1,2-benzenediamine) (Peng & Liaw, 1986). They postulate that it is formed *via* *o*-benzoquinonediimine as an intermediate. They also find protonation on an aromatic N atom, without giving any details.



(I)

The numbering scheme and the geometry of the molecule are shown in Fig. 1. Of the 18 directly bonded C—C or C—N distances, there are five where the disagreement is greater than 3σ. In each case, the difference arises from the greater asymmetry of bond lengths between the protonated and unprotonated sides of the cation, as found by Peng & Liaw (1986). This could possibly arise from the position of the anions.

The organic portion is essentially planar (Table 3). The C—C and C—N bond lengths of the unsubstituted side of the molecule agree closely with those found for phenazine (Herbstein & Schmidt, 1955; Wozniak, Kariuki & Jones, 1991). The corresponding bond lengths on the amino-substituted side of the molecule differ from those observed for *o*-phenylenediamine (Stahlhandske, 1981).

The crystal is stabilized by a complex hydrogen-bonding network that extends from the Cl atom to the two water molecules (*W*1 and *W*2), whose H atoms were found directly, then on to adjacent layers (*W*1 to the non-protonated ring atom N1, and *W*2 to another *W*1), and from the Cl atom to the N3—H and N4—H groups, then on to adjoining layers (N3 to another Cl and N4 to another *W*2). The third water molecule, *W*3, for which only one H atom was found directly, appears to be hydrogen bonded to the protonated ring atom N3.

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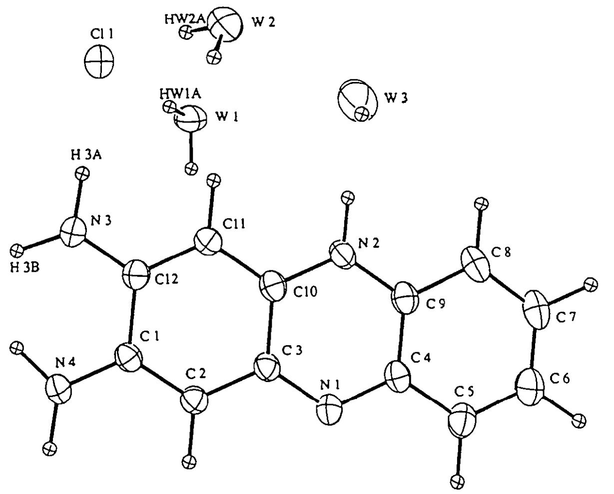

Fig. 1. An *ORTEP*II (Johnson, 1976) plot with 50% probability ellipsoids of 2,3-diamino-5-hydrophenazinium chloride trihydrate.

Experimental

1.22 g of 1,2-benzenediamine (11.4 mol eq.) dissolved in 20 ml of chloroform was added, with rapid stirring, to 0.894 g of acetyl chloride (11.4 mol eq.) dissolved in 20 ml of chloroform. A white precipitate formed immediately. This was filtered, washed with a little chloroform and dried under vacuum to yield 1.31 g of crude product. This was dissolved in water to give a pale yellow acidic solution from which a small quantity of red needles slowly crystallized.

Crystal data

$C_{12}H_{11}N_4^+.Cl^-.3H_2O$
$M_r = 300.74$
Triclinic
$P\overline{1}$
$a = 6.8102\,(14)$ Å
$b = 9.8841\,(18)$ Å
$c = 11.2926\,(18)$ Å
$\alpha = 74.487\,(16)°$
$\beta = 77.343\,(15)°$
$\gamma = 83.580\,(23)°$
$V = 713.50\,(23)$ Å^3
$Z = 2$
$D_x = 1.400$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 40$–$55°$
$\mu = 2.51$ mm^{-1}
$T = 278$ K
Needle
0.41 × 0.035 × 0.035 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2495 measured reflections
1764 independent reflections
1316 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 54.8°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 10$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 1.5% (long term)

Refinement

Refinement on F
$R = 0.060$
$wR = 0.070$

$(\Delta/\sigma)_{\rm max} = 0.017$
$\Delta\rho_{\rm max} = 0.250$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.280$ e Å^{-3}

$S = 2.30$
1316 reflections
181 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.005F^2]$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl1	0.3991 (2)	0.77988 (15)	0.90323 (13)	5.38 (8)
N1	0.7990 (6)	0.4747 (4)	0.3582 (3)	3.5 (2)
N2	0.7334 (6)	0.7311 (4)	0.4199 (4)	3.6 (2)
N3	0.6482 (7)	0.4948 (4)	0.8535 (4)	4.4 (2)
N4	0.7167 (6)	0.2375 (4)	0.7920 (4)	4.0 (2)
C1	0.7200 (7)	0.3570 (5)	0.6996 (4)	3.4 (2)
C2	0.7584 (7)	0.3544 (5)	0.5751 (4)	3.4 (2)
C3	0.7624 (7)	0.4792 (5)	0.4783 (4)	3.2 (2)
C4	0.8035 (7)	0.5974 (5)	0.2660 (4)	3.4 (2)
C5	0.8412 (8)	0.5947 (6)	0.1389 (5)	4.3 (3)
C6	0.8464 (8)	0.7169 (6)	0.0482 (5)	4.9 (3)
C7	0.8126 (9)	0.8466 (6)	0.0796 (5)	5.0 (3)
C8	0.7737 (8)	0.8542 (5)	0.2012 (5)	4.4 (3)
C9	0.7698 (7)	0.7283 (5)	0.2968 (4)	3.7 (2)
C10	0.7265 (7)	0.6122 (5)	0.5124 (4)	3.3 (2)
C11	0.6867 (7)	0.6155 (5)	0.6381 (4)	3.5 (3)
C12	0.6837 (7)	0.4927 (5)	0.7318 (4)	3.4 (2)
O1	0.1257 (6)	0.7872 (4)	0.7129 (3)	5.4 (2)
O2	0.7594 (6)	0.9588 (4)	0.7334 (3)	5.7 (2)
O3	0.7328 (9)	0.9816 (5)	0.4838 (5)	10.3 (4)

Table 2. *Selected geometric parameters* (Å, °)

N1—C3	1.336 (6)	C3—C10	1.447 (6)
N1—C4	1.369 (6)	C4—C5	1.408 (7)
N2—C9	1.364 (6)	C4—C9	1.410 (7)
N2—C10	1.345 (6)	C5—C6	1.357 (8)
N3—C12	1.347 (6)	C6—C7	1.401 (9)
N4—C1	1.350 (6)	C7—C8	1.360 (8)
C1—C2	1.379 (6)	C8—C9	1.412 (7)
C1—C12	1.463 (6)	C10—C11	1.394 (6)
C2—C3	1.411 (6)	C11—C12	1.379 (7)
C3—N1—C4	119.7 (4)	C2—C1—C12	119.1 (4)
C9—N2—C10	121.7 (4)	C1—C2—C3	121.6 (4)
N4—C1—C2	121.5 (4)	N1—C3—C2	120.8 (4)
C6—C7—C8	121.3 (5)	N1—C3—C10	120.9 (4)
C7—C8—C9	118.9 (5)	C2—C3—C10	118.3 (4)
N2—C9—C4	119.1 (4)	N1—C4—C5	120.5 (4)
N2—C9—C8	120.8 (4)	N1—C4—C9	120.5 (4)
C4—C9—C8	120.1 (4)	C5—C4—C9	119.0 (4)
N2—C10—C3	118.1 (4)	C4—C5—C6	120.1 (5)
N2—C10—C11	121.5 (4)	C5—C6—C7	120.6 (5)
C3—C10—C11	120.4 (4)	N3—C12—C1	118.9 (4)
C10—C11—C12	120.8 (4)	N3—C12—C11	121.3 (4)
N4—C1—C12	119.4 (4)	C1—C12—C11	119.9 (4)

Table 3. *Distances* (Å) *to the least-squares plane*

Equation of the plane: $6.80144\,(17)x + 1.307\,(10)y + 2.034\,(7)z = 6.788\,(9)$.

Distances to the plane from the atoms in the plane

N1	−0.004 (4)	N2	0.009 (5)
N3	0.003 (5)	N4	0.009 (5)
C1	−0.001 (5)	C2	0.003 (5)
C3	−0.003 (5)	C4	−0.001 (5)
C5	−0.007 (6)	C6	0.004 (7)
C7	0.007 (7)	C8	−0.001 (6)
C9	0.003 (5)	C10	−0.004 (5)
C11	−0.015 (5)	C12	−0.005 (5)

Distances to the plane from the atoms out of the plane

Cl1	−1.217 (5)	O1	−3.455 (6)
O2	1.122 (7)	O3	0.463 (8)

The high R value is due to the small crystal size. Computations were carried out using programs of the *NRCVAX* package (Gabe, Le Page, Charland, Lee & White, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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17β-Hydroxy-3-methoxyestra-1,3,5(10)-triene-6,7-dione 7-Oxime

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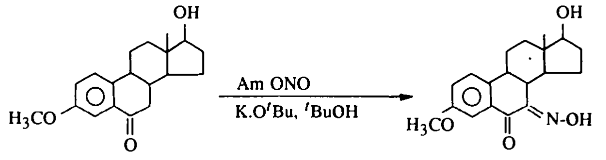
Abstract

X-ray structure analysis of the title compound, $C_{19}H_{23}NO_4$, showed an unexpected *anti* orientation for the 6-oxo-7-oximino function. After molecular-mechanics calculations, the H atom of the 17-hydroxy moiety, which participates in a strong hydrogen bond formed in the crystalline state, changed its orientation substantially. Some change in the conformation of ring B was also observed.

Comment

To prepare a suitably functionalized estradiol derivative for further chemical transformations into a 6,7-seco steroid system, synthesis of 17β-hydroxy-3-methoxyestra-1,3,5(10)-triene-6,7-dione 7-oxime was carried out by the base-catalysed action of amyl nitrate on 17β-hydroxy-3-methoxyestra-1,3,5(10)-triene-6-one, (1):



(1) (2)

The chemical structure of (2) was deduced by spectroscopic data (the ^{1}H NMR spectrum showed a signal at 11.65 p.p.m., corresponding to HO—N<; the signal in the ^{13}C NMR spectrum at 153.18 p.p.m. originates from C7=N—OH), but the exact geometry of the oximino function still remained undefined. Therefore, an X-ray structural analysis of the title compound was undertaken.

From the analysis, it was found that compound (2) possesses the *anti* geometry for the 6-oxo-7-oximino function. In addition, molecular-mechanics calculations were performed to establish possible changes in the conformation and distances between the functional groups in the molecule of (2) when released from the interactions with surrounding molecules in the crystalline state.

A perspective view of the molecule, computed from the final atomic coordinates listed in Table 1, is shown in Fig. 1. Unusually high displacement factors for the O4 atom were found. Ring-puckering parameters (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976), listed in Table 3, define the ring conformations (Fig. 2).

Ring B exhibits an 8β-envelope (sofa) conformation. The distance of C8 from the best plane of the remaining five atoms is 0.696 (5) Å. Ring C has an 8β,12α-chair conformation, while the five-membered ring D adopts a 13β,14α-half chair conformation [the distances of C13 and C14 from the best plane of the remaining three atoms are 0.499 (5) and −0.316 (5) Å, respectively], slightly distorted towards a 13β-envelope conformation. After energy minimization, there were no noticeable changes in the conformation of rings C and D. However, the envelope conformation of ring B, the only

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