

O(2)(B) are 2.773 and 2.175 Å, respectively. These values are somewhat larger than the corresponding values of 2.754 and 1.98 Å and 2.775 and 1.980 Å for the tropolone dimer and the 5-isopropyltropolone dimer, respectively. This implies that the substitution of a Cl atom in the 3-position of the ring has slightly weakened the strength of the intermolecular hydrogen bond.

The hydroxylic proton has been found to be delocalized in the isolated 3-chlorotropolone (Tsuji, Sekiya, Nishimura, Mori & Takeshita, 1991) and tropolone (Tomioka, Mikami & Ito, 1983), whereas the hydroxylic proton is localized on the O atom in crystalline 3-chlorotropolone and tropolone (Shimanouchi & Sasada, 1973). The localization of the hydroxylic proton in crystalline tropolone and 3-chlorotropolone suggests that the effective potential energy barrier to proton tunneling has increased due to the formation of the intermolecular hydrogen bonds.

The measurement and the analysis of the data were carried out in the Center of Advanced Instrumental Analysis, Kyushu University. One of the authors (HS) wishes to thank Dr Hirofumi Sakashita (Center of Instrumental Analysis) for valuable discussions.

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Structure of 1-Ethyl-5-nitroimidazole Hydrochloride Monohydrate at 100 K

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Abstract. $C_5H_8N_3O_2^+ \cdot Cl^- \cdot H_2O$, $M_r = 195.60$, orthorhombic, $P2_12_12_1$, $a = 6.436$ (3), $b = 11.023$ (7), $c = 12.482$ (7) Å, $V = 885.6$ (9) Å³, $Z = 4$, $D_m = 1.46$, $D_x = 1.467$ Mg m⁻³, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.403$ mm⁻¹, $F(000) = 408$, $T = 100$ K, final $R = 0.020$ for 1038 unique observed [$F \geq 4\sigma(F)$] reflections. Protonation of N3 is responsible for the opening of the N3 ring angle relative to the corresponding average angle of the

unprotonated 5-nitroimidazoles or to N3 in imidazole. The influence of the N3 proton substituent on the unsubstituted C2 and C4 *ortho* ring angles is opposite to its influence on the *ipso* angle. The nitro group makes an angle of 13.9° to the imidazole ring. The intermolecular hydrogen bonds build up a helix parallel to the a axis.

Introduction. Nitroimidazoles are generally known as antiprotozoic and antibiotic drugs (Edwards, 1981). The investigation of 1-ethyl-5-nitroimidazole hydrochloride monohydrate is part of an extensive structure–activity study including conformational

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analysis on room-temperature data as well as charge-density analysis on high-resolution data sets (De Bondt, Blaton, Peeters, De Ranter & Kj oller-Larsen, 1991).

Experimental. Colourless crystals were selected directly from the sample (Merck, Sharp & Dohme Research Laboratories, Rahway, New Jersey, USA) and were used for density measurements by flotation in *n*-heptane/CCl₄. A prismatic crystal with approximate dimensions of 0.2 × 0.2 × 0.3 mm was mounted for X-ray diffraction data collection on a Stoe Stadi-4 four-circle diffractometer with graphite-monochromated Mo Kα (reflection 200) radiation. Severe damage by exposure to X-rays at room temperature was prevented by cooling down to 100 K. The space group, *P*₂₁₂₁, was determined from observed symmetry and systematic absences *h*00 (*h* = 2*n*), 0*k*0 (*k* = 2*n*), 00*l* (*l* = 2*n*). Unit-cell dimensions were obtained by least-squares refinement of the setting angles of 24 reflections with 18 ≤ 2θ ≤ 21°. X-ray intensities were collected in the ω/2θ scan mode up to maximal (sinθ)/λ = 0.65 Å⁻¹, corresponding to 2θ_{max} = 55° and for 0 ≤ *h* ≤ 8, -14 ≤ *k* ≤ 0, -16 ≤ *l* ≤ 16. Friedel pairs were not collected. For all reflections, peak profiles of 96 steps were stored. Intensities of three standard reflections (312, 232, 135), monitored every 2 h of radiation, showed an average decrease in intensity of 0.6% in 66 h radiation. The reflection intensities were rescaled using a cubic regression curve. A total of 2303 reflections were measured. Symmetry-related reflections were averaged to give 1103 unique reflections (*R*_{int,observed,*F*} = 0.016) of which 1038 were considered observed with *F* ≥ 4σ(*F*). Data reduction with the peak profile analysis program *DREAM* (Blessing, 1987). Lorentz and polarization corrections were applied. The observation of negligible absorption as a function of ψ for three reflections (211, 312, 521) justified the omission of absorption corrections. Structure factors were calculated with scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) and contracted hydrogen form factors from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were performed for all non-H atoms (Ibers & Hamilton, 1964). The phase problem was successfully solved by direct methods using *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) which revealed the positions of all non-H atoms. Full-matrix least-squares refinements were performed on *F*, first isotropically and next anisotropically. The ten H atoms were located in a difference map. Hydrogen positions were refined with *B* fixed at 1.5 Å². *w* = 4*F*²/[σ²(*F*²) + (0.02*F*²)²]. Final *R* = 0.020, *wR* = 0.024, with *S* = 1.26. Largest parameter shift/e.s.d. = 0.03. The residual electron

density varies between -0.13 and 0.12 e Å⁻³. The number of reflections per refined parameter was 1038/139 = 7.5. All calculations were performed on a Digital PDP-11/73 and MicroVAX 2000 micro-computer using *SDP/VAX* (Frenz, 1985) and *PARST* (Nardelli, 1983).

Discussion. An *ORTEPII* view (Johnson, 1976) of the title compound with the atomic numbering scheme is shown in Fig. 1. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths, bond angles and selected torsion angles are given in Table 2.* Compared to other 5-nitroimidazoles (Bales, Mazid, Sadler, Aggarwal, Kuroda, Neidle, Gilmour, Peart & Ramsden, 1985; Blaton, Peeters & De Ranter, 1979*a,b*; Chasseaud, Henrick, Matthews, Scott & Wood, 1984; Germain, Declercq & Van Meerssche, 1977; all of them are unprotonated at N3), the ring angle at the protonated N3, 109.2 (1)°, is significantly more obtuse. This ring angle is also more obtuse than N3 [105.1 (1)°] in imidazole itself (McMullan, Epstein, Ruble, Craven, 1979). The ring angles at C2 and C4 [109.7 (2) and 105.8 (1)°] however, are more acute than the corresponding mean values of 111.3 (3) and 109.2 (6)° and than those in unsubstituted imidazole [111.9 (1) and 109.8 (1)°]. The ring deformation patterns in polysubstituted benzene derivatives (Domenicano, Murray-Rust & Vacigo, 1983) are also valid for the title compound. The angular changes occurring at the *ipso* and the *ortho* positions of the benzene ring are controlled

* Lists of structure factors, anisotropic thermal parameters and details of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54313 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

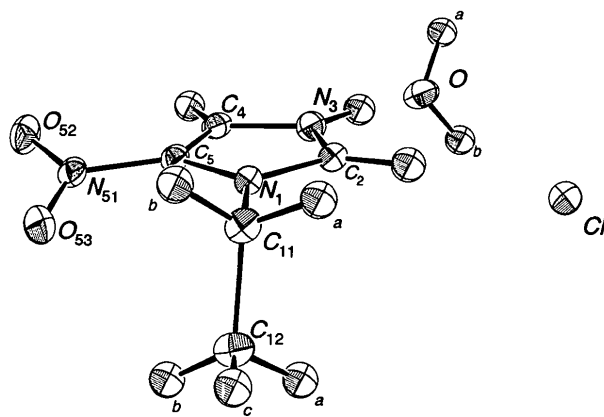


Fig. 1. An *ORTEP* plot (Johnson, 1976) of the title compound with atomic numbering scheme. The ellipsoids enclose 50% probability.

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å² × 10²)

E.s.d.'s on least significant digit are given in parentheses.

$$U_{eq} = (1/3) \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
N1	0.3755 (2)	0.0383 (1)	0.5628 (1)	1.25 (3)
C2	0.5123 (3)	0.0485 (2)	0.6417 (1)	1.49 (4)
N3	0.4458 (2)	0.1299 (1)	0.7125 (1)	1.56 (3)
C4	0.2578 (3)	0.1733 (2)	0.6806 (1)	1.43 (4)
C5	0.2141 (3)	0.1162 (2)	0.5871 (1)	1.29 (4)
C11	0.4050 (3)	-0.0444 (2)	0.4699 (1)	1.56 (4)
C12	0.4938 (3)	0.0214 (2)	0.3741 (1)	1.90 (4)
N51	0.0335 (2)	0.1339 (1)	0.5225 (1)	1.60 (4)
O52	-0.1105 (2)	0.1887 (1)	0.5644 (1)	2.24 (3)
O53	0.0343 (2)	0.0954 (1)	0.4305 (1)	2.31 (3)
Cl	0.93146 (7)	-0.14212 (4)	0.61192 (3)	1.50 (1)
O	0.6515 (2)	0.2136 (1)	0.8758 (1)	2.36 (4)
H2	0.640 (3)	0.001 (2)	0.645 (2)	1.9*
H3	0.512 (3)	0.151 (2)	0.769 (2)	1.9*
H4	0.187 (3)	0.234 (2)	0.722 (2)	1.9*
H11A	0.499 (3)	-0.107 (2)	0.497 (2)	1.9*
H11B	0.271 (3)	-0.080 (2)	0.457 (2)	1.9*
H12A	0.622 (3)	0.062 (2)	0.395 (2)	1.9*
H12B	0.412 (4)	0.084 (2)	0.346 (2)	1.9*
H12C	0.516 (4)	-0.038 (2)	0.317 (2)	1.9*
HA	0.636 (3)	0.195 (2)	0.935 (2)	1.9*
HB	0.749 (3)	0.253 (2)	0.874 (2)	1.9*

* Temperature factors were fixed at $U = 1.9 \times 10^{-2} \text{ \AA}^2$.

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°)

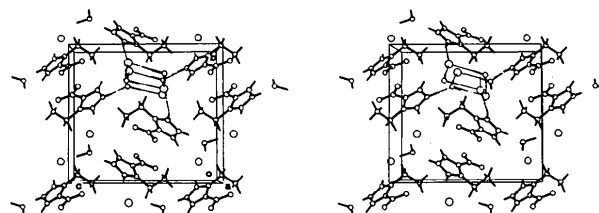
E.s.d.'s on least significant digit are given in parentheses.

N1—C2	1.326 (2)	C5—N51	1.429 (2)
C2—N3	1.330 (2)	N51—O52	1.224 (2)
N3—C4	1.361 (2)	N51—O53	1.225 (2)
C4—C5	1.356 (2)	C11—H11A	0.98 (2)
C5—N1	1.381 (2)	C11—H11B	0.96 (2)
N1—C11	1.487 (2)	C12—H12A	0.97 (2)
C11—C12	1.510 (3)	C12—H12B	0.94 (2)
C4—H4	0.96 (2)	C12—H12C	0.98 (2)
O—HA	0.78 (2)	C2—H2	0.98 (2)
O—HB	0.77 (2)	N3—H3	0.86 (2)
C2—N1—C5	106.4 (1)	C5—C4—H4	134 (1)
C2—N1—C11	123.1 (2)	N1—C5—C4	108.8 (2)
C5—N1—C11	130.4 (2)	N1—C5—N51	124.9 (1)
N1—C2—N3	109.7 (2)	C4—C5—N51	126.2 (2)
N1—C2—H2	123 (1)	N1—C11—C12	111.8 (1)
N3—C2—H2	127 (1)	N1—C11—H11A	104 (1)
C2—N3—C4	109.2 (1)	N1—C11—H11B	105 (1)
C2—N3—H3	125 (1)	C12—C11—H11A	112 (1)
C4—N3—H3	126 (1)	C12—C11—H11B	114 (1)
N3—C4—C5	105.8 (1)	H11A—C11—H11B	109 (2)
N3—C4—H4	120 (1)	C11—C12—H12A	110 (1)
C11—C12—H12B	116 (1)	C5—N51—O52	116.3 (1)
C11—C12—H12C	108 (1)	C5—N51—O53	118.6 (2)
H12A—C12—H12B	104 (2)	O52—N51—O53	125.1 (1)
H12A—C12—H12C	112 (2)	HAO—HB	106 (2)
H12B—C12—H12C	107 (2)		
H3—N3—C4—C5	179 (2)	C2—N1—C11—C12	-96.9 (2)
C5—N1—C2—H2	178 (1)	C4—C5—N51—O52	-14.0 (2)
C11—N1—C2—N3	179.2 (1)	C4—C5—N51—O53	165.2 (2)
H4—C4—C5—N1	178 (2)	C5—N1—C11—C12	83.5 (2)
C2—N1—C5—N51	179.6 (2)	N1—C2—N3—C4	1.1 (2)
C11—N1—C5—C4	-179.7 (2)	N1—C2—N3—H3	-179 (2)
N1—C5—N51—O52	167.2 (2)	H2—C2—N3—C4	-178 (2)
N1—C5—N51—O53	-13.6 (2)	C2—N3—C4—H4	-179 (1)

Table 3. Geometry of intra- and intermolecular hydrogen bonds (Å, °)

E.s.d.'s on least significant digit are given in parentheses. H-atom positions are normalized to C—H = 1.08, N—H = 1.01 and O—H = 0.96 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

Donor—H	Donor...Acceptor	H...Acceptor	Donor—H...Acceptor
C2—H2	C2...Cl (i)	H2...Cl (i)	C2—H2...Cl (i)
1.08	3.448 (2)	2.391 (2)	165.9 (2)
N3—H3	N3...O (i)	H3...O (i)	N3—H3...O (i)
1.01	2.605 (2)	1.602 (2)	172.4 (2)
O—HA	O...Cl (ii)	HA...Cl (ii)	O—HA...Cl (ii)
0.96	3.104 (2)	2.144 (2)	176.4 (2)
O—HB	O...Cl (iii)	HB...Cl (iii)	O—HB...Cl (iii)
0.96	3.131 (2)	2.178 (2)	172.3 (2)

Symmetry code: (i) x, y, z ; (ii) $-x + \frac{1}{2} + 1, -y, z + \frac{1}{2}$; (iii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2} + 1$.Fig. 2. A PLUTO plot (Motherwell & Clegg, 1978) of the crystal showing the packing along *a*. Thin lines indicate hydrogen bonds.

primarily by the inductive effects of the substituents. In particular, because of the *ipso* protonation, the N3 ring angle is opened relative to the corresponding average angle of the unprotonated 5-nitroimidazoles or to N3 in imidazole itself. The influence of the N3 proton substituent on the unsubstituted C2 and C4 *ortho* ring angles is opposite to its influence on the *ipso* angle. Consequently, there is a marked closing effect at C2 and at C4. The σ -electron-withdrawing nitro substituent increases the *ipso* ring angle from 106.0 (1) to 108.8 (2)°. The imidazole ring is almost planar with a maximum deviation from the best least-squares plane of 0.008 (2) Å. The dihedral angle between the least-squares plane through the imidazole and the nitro group is 13.9 (2)°. Fig. 2 shows the stacking along the *a* axis. Inspection of non-bonding distances shorter than the sum of the van der Waals radii reveals the hydrogen bonds summarized in Table 3. The intermolecular hydrogen bonds set up a hydrogen-bond helix parallel to the *a* axis.

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SHORT-FORMAT PAPERS

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Acta Cryst. (1991). **C47**, 2433–2435

Structure of Gadolinium Hexacyanoferrate(III) Tetrahydrate

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Abstract. $\text{GdFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, $M_r = 441.26$, orthorhombic, $Cmcm$, $a = 7.3964$ (3), $b = 12.8372$ (5), $c = 13.6726$ (4) Å, $V = 1298.21$ (8) Å³, $Z = 4$, $D_m = 2.23$ (2), $D_x = 2.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 6.223$ mm⁻¹, $F(000) = 832$, $T = 291$ K, final $R = 0.016$ for 1017 absorption-corrected unique reflections with $F_o \geq 6\sigma|F_o|$. The eight-coordinated Gd ion is bonded to six cyano N atoms and two water molecules in a square antiprism geometry (D_{4d}), the $\text{GdN}_6(\text{H}_2\text{O})_2$ group. The Fe ion is octahedrally coordinated to six cyano C atoms, the FeC_6 group. Cyanide bridging links these groups to build an infinite polymeric array. Cavities within the structure are occupied by uncoordinated zeolitic water molecules, O(1), which are within hydrogen-bonding distances (2.818 Å) to the coordinated water molecules, O(1). Important mean bond distances are: Gd—N

$= 2.489$ (14); Fe—C = 1.927 (4); and C≡N = 1.152 (1) Å.

Experimental. Crystals of $\text{GdFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ were synthesized by a procedure similar to that of Prandtl & Mohr (1938). An aqueous acidic solution (pH = 4.0) of 0.2M GdCl_3 was added to 15 ml of 0.1M $\text{K}_3\text{Fe}(\text{CN})_6$. The mixture was stirred, filtered and stored in the dark at room temperature. Clear dark-red crystals formed after three to five days. The metal constituents and their ratios were verified by X-ray fluorescence analysis on a Novascan 30 SEM. The water content was confirmed by thermal gravimetric analysis (TGA), 3.9 (1) H₂O molecules/formula unit. The flotation method (bromobenzene and 1,1,2,2-tetrabromoethane) was employed to determine the experimental density. Infrared spec-