Fig. 3. Coordination of barium atoms (broken lines). Oxygen atoms are identified only by numbers. For the symmetry-operation superscripts see Table 5.

Table 5. *Interatomic distances* (Å) *between* Ba *and* O *atoms and between metal atoms*

Ba–O

	Ba(1)		Ba(2)
O(1^i)	2·95 (2)	O(1^i)	2·67 (2)
O(2^{ii})	2·76 (2)	O(2)	2·79 (2)
O(3)	2·81 (2)	O(2^v)	2·64 (2)
O(4)	3·05 (2)	O(3)	2·74 (2)
O(4^{iii})	2·76 (2)	O(4^{iii})	2·83 (2)
O(5^{iv})	2·80 (2)	O(5^i)	3·05 (2)
O(6^{iii})	2·91 (2)	O(6^i)	2·85 (2)
O(7)	2·75 (2)	O(8)	2·52 (2)
O(8^{ii})	2·72 (2)		
Average	2·83	Average	2·76
Next nearest neighbour		Next nearest neighbour	
O(1^{iii})	3·20 (2)	O(7^{iv})	3·37 (2)

Ba——Ba	Min.	3·878 (4)
W——W	Min.	3·219 (3)
Ba(1)–W(1)		3·713 (3)
Ba(2)–W(2)		3·603 (3)

Symmetry code

i	$x,$	$1+y,$	z
ii	$x,$	$y,$	$-1+z$
iii	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$
iv	$-x,$	$1-y,$	$1-z$
v	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	$\frac{3}{2}-z$

The calculations were carried out on the FACOM 270-20 of the National Institute for Researches in Inorganic Materials. Bond lengths and angles were calculated using the program *ORFFE* (Busing, Martin & Levy, 1964).

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3,5-Dinitropyridine

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Abstract. 3,5-Dinitropyridine, $C_5H_3N_3O_4$, is orthorhombic, space group $P2_12_12_1$; $a=19\cdot918(3)$, $b=6\cdot465(1)$, $c=5\cdot272(1)$ Å, $Z=4$, $D_m=1\cdot65$, $D_c=1\cdot654$ g cm^{-3}. One of the two nitro groups is approximately coplanar with the ring system; the other is rotated by 7°. This small but significant rotation is very likely due to packing interactions.

Introduction. Crystals of 3,5-dinitropyridine are pale yellow prisms elongated along the chosen crystallo-graphic *b* axis. The cell dimensions were obtained by a least-squares fit to the $\sin^2\theta$ values of 48 *hkl* reflexions measured on a diffractometer. The density was measured by flotation in dilute Thoulet (K_2HgI_4) solution. Crystal data are given in Table 1. For the data collection, a crystal with approximate dimensions 0·40 × 0·20 × 0·15 mm was sealed in a Lindemann-glass capillary. Intensities were collected on a Syntex automated diffractometer with Mo $K\alpha$ radiation [λ (Mo $K\alpha$) = 0·7107 Å; graphite monochromator] and a variable

rate θ–2θ scan technique ($2\theta_{max} = 54\cdot6°$). Three check reflexions were measured after every 25 reflexions and showed no significant change.

Table 1. *Crystal data*

$C_5H_3N_3O_4$	F.W. 169·1
Space group $P2_12_12_1$	λ (MoKα) = 0·7107 Å
$a = 19\cdot918$ (3) Å	μ (MoKα) = 1·57 cm^{-1}
$b = 6\cdot465$ (1)	$Z = 4$
$c = 5\cdot272$ (1)	$D_c = 1\cdot654$ g cm^{-3}
$V = 678\cdot9$ (3) Å^3	$D_m = 1\cdot65$ (1) g cm^{-3}
$F(000) = 344$	

928 independent reflexions were measured, of which 30 had negative values for their net intensities. Each reflexion was assigned a variance of $\sigma^2(I)$ based on counting statistics plus a term $(0\cdot02\ S)^2$, where S is the scan count [see, for example, Peterson & Levy (1957)]. Intensities and their standard deviation $\sigma(I)$ were corrected for Lorentz and polarization factors, but not for absorption ($\mu r_{max} < 0\cdot1$).

The structure was solved by direct methods, based on the 137 reflexions with $E \geq 1\cdot40$, with a set of programs written by Bianchi, Destro & Gavezzotti (1972) [see also Destro, Kistenmacher & Marsh (1972)]. The resulting E map showed the location of all non-hydrogen atoms, which led to an R ($= \Sigma|F_o - F_c|/\Sigma|F_o|$) of $0\cdot277$ for the 928 measured reflexions. After four cycles of full-matrix least-squares adjustment of the coordinates and isotropic temperature factors ($R = 0\cdot149$), a difference map indicated the location of the hydrogen atoms. Final refinement cycles included in a single matrix 121 parameters: coordinates for all 15 atoms, anisotropic thermal parameters for the 12 heavy atoms, isotropic B's for the 3 hydrogen atoms and a scale factor. The final R was $0\cdot046$ for 898 reflexions having net intensities greater than zero ($0\cdot049$ including rejects), the weighted $R\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}\}$ $0\cdot041$, and the goodness-of-fit $\{= [\Sigma w(|F_o| - |F_c|)^2/(m - s)]^{1/2}\}$ for $m = 928$ observations and $s = 121$ parameters, $1\cdot53$. The largest shift in the final least-squares calculation was $0\cdot5\sigma$. A final difference map showed a
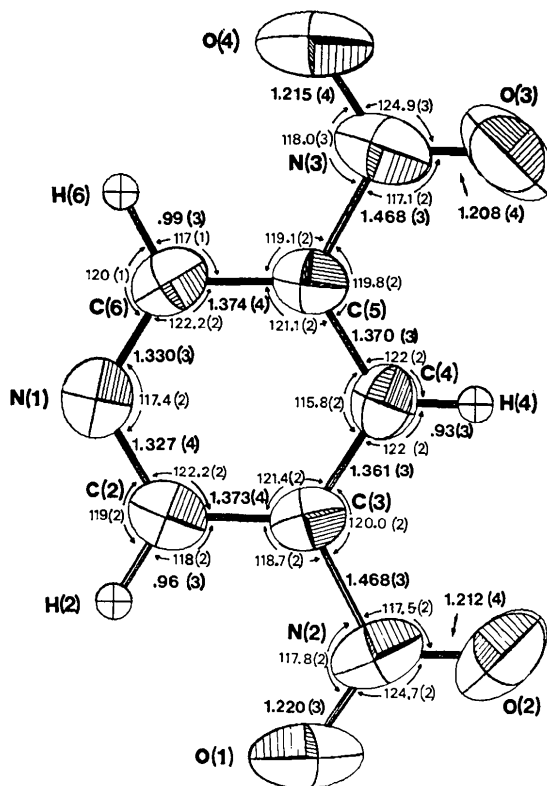

Fig. 1. The 3,5-dinitropyridine molecule. The atoms are represented by temperature-factor ellipsoids drawn at the 50% probability level (Johnson, 1965).

maximum value of $0\cdot35$ e Å^{-3}, located near the O(4) atom.

Atomic form factors were from Cromer & Waber (1965), except those for H which were from Stewart, Davidson & Simpson (1965). The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, with weights w taken equal to $1/\sigma^2(F_o)$ [where $\sigma^2(F_o) = \sigma^2(F_o^2)/4F_o^2$], except for the 30 reflexions having $I < 0$, for which $w = 0$. A modified version of *ORFLS* (Busing, Martin & Levy, 1962) was

Table 2. *Final atomic parameters and standard deviations* (*in parentheses*)

The anisotropic temperature coefficients are in the form $T_i = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$. Fractional coordinates are $\times 10^5$ for heavy atoms, $\times 10^3$ for hydrogen atoms. Anisotropic temperature coefficients are $\times 10^4$, isotropic B's $\times 10$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	18321 (11)	54688 (35)	92496 (46)	37 (1)	317 (6)	438 (9)	9 (2)	−28 (2)	−61 (7)
C(2)	19202 (13)	37562 (40)	79017 (52)	27 (1)	244 (6)	442 (11)	12 (2)	−1 (2)	26 (8)
C(3)	15387 (10)	33113 (32)	58020 (48)	22 (1)	178 (5)	376 (9)	−7 (1)	22 (2)	−5 (7)
C(4)	10485 (11)	46190 (34)	49900 (48)	21 (1)	225 (6)	359 (9)	−16 (1)	0 (2)	−10 (6)
C(5)	9655 (10)	63847 (32)	63910 (46)	19 (1)	193 (5)	429 (10)	−3 (1)	11 (2)	18 (6)
C(6)	13539 (12)	67647 (39)	84941 (51)	32 (1)	224 (6)	411 (11)	3 (2)	5 (2)	−63 (7)
N(2)	16656 (11)	13727 (31)	44341 (51)	33 (1)	202 (5)	534 (11)	−6 (2)	39 (2)	−70 (7)
N(3)	4548 (11)	79044 (34)	56453 (61)	25 (1)	248 (6)	736 (14)	11 (2)	7 (3)	75 (9)
O(1)	20592 (12)	1465 (32)	53725 (48)	54 (1)	257 (5)	805 (12)	42 (2)	38 (3)	−12 (8)
O(2)	13672 (11)	10993 (34)	24590 (51)	54 (1)	364 (7)	641 (11)	−12 (2)	3 (3)	−220 (8)
O(3)	1342 (12)	75354 (35)	37552 (66)	50 (1)	393 (7)	1118 (18)	22 (2)	−120 (4)	96 (10)
O(4)	3913 (11)	94443 (33)	69428 (51)	43 (1)	320 (5)	914 (15)	49 (2)	41 (3)	−32 (8)

Table 2 (*cont.*)

	x	y	z	B
H(2)	227 (1)	280 (4)	838 (6)	64 (7)
H(4)	77 (1)	430 (4)	365 (6)	63 (7)
H(6)	126 (1)	805 (4)	947 (5)	55 (6)

used for the full-matrix least-squares refinement.* Fig. 1 was produced, in part, by *ORTEP* (Johnson, 1965). The final parameters are given in Table 2.

Discussion. The numbering of atoms is shown on the thermal ellipsoids plot of Fig. 1, which includes bond distances and angles. The uncertainties in the coordinates (Table 2) correspond to standard deviations in the range 0·0030–0·0043 Å in the bond lengths and 0·20–0·31° in the bond angles involving only heavier atoms. Although the e.s.d.'s derived from X-ray analysis are usually to be viewed with some scepticism, the comparison between chemically equivalent bond distances and angles in 3,5-dinitropyridine suggests that the values quoted above are realistic. To rationalize this impression we have evaluated the root-mean-square value of the quantity $\Delta m / \sigma(\Delta m)$, where Δm is the observed difference within each of the 13 pairs of equivalent (assuming m symmetry) bond distances and angles, and $\sigma(\Delta m)$ is the calculated e.s.d. of this difference; the resulting 'goodness-of-fit' value is 1·0, confirming that the coordinate e.s.d.'s have not been underestimated.

The effects of the nitro groups at C(3) and C(5) on the bond distances and angles of the pyridine system are seen by comparing the values found here with those reported by Bak, Hansen-Nygaard & Rastrup-Andersen (1958) who observed by microwave spectroscopy bond distances of 1·3402 for N(1)–C(2) and N(1)–C(6), 1·3944 for C(2)–C(3) and C(5)–C(6), and 1·3945 Å for C(3)–C(4) and C(4)–C(5); the bond angles were 116·83° at N(1), 123·88° at C(2) and C(5), 118·53° at C(3) and C(5), and 118·33° at C(4).

The atoms of the pyridine ring are coplanar within 0·005 Å (Table 3). The nitro group bonded to C(5) is nearly coplanar with the pyridine ring (angle between the planes = 1·5°), while the other is significantly rotated, the dihedral angle between the corresponding planes being 7·0°. Packing interactions are presumably responsible for these rotations, since all but one [N(1)-C(2)] of the shortest intermolecular contacts (Table 4) involve oxygen atoms.

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30447 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Deviations from least-squares planes*

Plane 1 is the best plane through atoms N(1)–C(6) of the pyridine ring, all weighted equally; planes 2 and 3 are the best planes through atoms of the nitro groups and C atoms to which they are bonded [C(3) and C(5) respectively].

	Plane 1*	Plane 2†	Plane 3‡
N(1)	0·001	0·139	0·055
C(2)	0·002	0·143	0·043
C(3)	−0·001	−0·001	0·006
C(4)	−0·002	−0·152	−0·018
C(5)	0·004	−0·147	0·001
C(6)	−0·005	−0·012	0·027
N(2)	−0·012	0·003	−0·017
O(1)	−0·152	−0·001	−0·136
O(2)	0·110	−0·001	0·075
N(3)	0·021	−0·286	−0·005
O(3)	0·058	−0·372	0·002
O(4)	0·015	−0·288	0·002
H(2)	0·020	0·263	0·076
H(4)	−0·059	−0·303	−0·098
H(6)	−0·034	−0·049	0·006

* Direction cosines of plane normal: 0·6648, 0·4746, −0·5769; origin-to-plane distance, 1·290 Å.

† Direction cosines of plane normal: 0·7498, 0·4353, −0·4983; origin-to-plane distance, 1·706 Å.

‡ Direction cosines of plane normal: 0·6806, 0·4758, −0·5571; origin-to-plane distance, 1·395 Å.

Table 4. *Intermolecular contact distances* (Å)

N(1)–C(2)	$\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$	3·18
C(2)–O(2)	x	y	$1+z$	3·15
C(5)–O(4)	$-x$	$-\frac{1}{2}+y$	$\frac{3}{2}-z$	3·11
C(6)–O(1)	x	$1+y$	z	3·08
O(1)–H(2)	$\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$	2·56
O(2)–H(6)	x	$-1+y$	$-1+z$	2·53
O(3)–H(4)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	2·48

For each pair of atoms, the coordinates of the second atom are transformed as shown.

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